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FATE OF POLYNUCLEAR AROMATIC HYDROCARBONS IN REFINERY WASTE APPLIED TO SOIL

Working for a Better Environment

FATE OF POLYNUCLEAR AROMATIC HYDROCARBONS IN REFINERY WASTE APPLIED TO SOIL

PACE Report No. 88-1

Prepared for

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ABSTRACT

This report describes a study regarding the fate and persistence of PAH's in soil that had been previously treated with refinery wastes. The study was divided into three parts. The first part was a laboratory study in which refinery waste additions were made to soil taken from a refinery landfarm and the concentrations of oil and grease and target PAH's were monitored with time. The target PAH's were as follows; naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthrene, pyrene, chrysene, benzo(a)anthracene, benzo(b/k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene. In the second part of the study, the concentrations of these same chemicals were monitored in soil and groundwater at three operating refinery landfarm sites. In Part 3, the fate of benzo(a)pyrene, naphthalene and anthracene were studied in detail using ^{14}C-labelled compounds added to soil from a refinery landfarm site.

Parts 1 and 2 required conventional extraction, cleanup and analysis of samples, the efficiency of which proved to be extremely variable. In addition, loss of high molecular weight PAH from soil over a 200 day monitoring period was low and, with the high variability in analysis, could not be quantified. It was observed in both the laboratory and the field that low molecular weight PAH's were readily lost from soil, as had been observed in the pure compound study, while high molecular weight PAH persisted. More precise information was obtained using ^{14}C-labelled chemicals which confirmed that degradation of benzo(a)pyrene in soil occurred, although an extensive period of acclimation (80 days) was required. Substantial degradation of benzo(a)pyrene in a field situation may not be observed in one field season under temperate, subhumid climatic conditions as the effective length of the field season may be insufficient for both acclimation and degradation.

Of the 16 PAH's measured in this study, the following 8 PAH's were consistently found in landfarm soils with elevated PAH concentrations as compared to background levels; phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, benzo(a)anthracene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene. Of the groundwater samples that contained elevated PAH concentrations, anthracene and chrysene were most commonly identified, although concentrations of phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were also identified in samples at some sites.

RESUME

Ce rapport est une description d'une étude sur le devenir et la persistance des hydrocarbures aromatiques polynucléaires (HAP) dans le sol traité antérieurement avec des résidus de raffinerie. L'étude fut divisée en trois parties. La première partie a consisté en une étude en laboratoire comportant l'addition de résidus de raffinerie à du sol prélevé d'un dépotoir de raffinerie et le suivi chronologique des concentrations d'huile et de graisse et des HAP cibles. Les HAP cibles comprenaient les composés suivants: le naphtalène, l'acénaphtylène, l'acénaphtène, le fluorène, le phénanthrène, l'anthracène, le fluoranthène, le pyrène, le chrysène, le benzo(a)anthracène, le benzo(b/k)fluoranthène, le benzo(a)pyrène, l'indeno(1,2,3-c,d)pyrène, le dibenzo(a,h)anthracène et le benzo(g,h,i)pérylène. La deuxième partie de l'étude a comporté le suivi des concentrations de ces mêmes composés chimiques dans le sol et dans l'eau souterraine aux sites des dépotoirs de trois raffineries en exploitation. La troisième partie a comporté l'étude détaillée du benzo(a)pyrène, du naphtalène et de l'anthracène au moyen de composés marqués au ^{14}C ajoutés à du sol prélevé d'un dépotoir de raffinerie.

Les parties un et deux de l'étude ont fait appel aux méthodes classiques d'extraction, de nettoyage et d'analyse des échantillons dont l'efficacité s'est avérée extrêmement variable. En plus, le taux de disparition des HAP à poids moléculaire élevé dans le sol sur une période de suivi de 200 jours était très bas et, en raison de la grande variabilité de l'analyse, il était impossible de le quantifier. On a constaté dans le laboratoire et sur le terrain que les HAP à faible poids moléculaire se dégageaient facilement du sol conformément aux résultats observés lors de l'étude des composés purs, tandis que les HAP à poids moléculaire élevé persistaient. On a obtenu, au moyen des composés chimiques marqués au ^{14}C, des données plus précises confirmant que le benzo(a)pyrène dans le sol subissait une dégradation, bien qu'une période prolongée d'acclimatation (80 jours) était nécessaire. Il est possible qu'une dégradation substantielle du benzo(a)pyrène ne soit pas observée au cours d'une seule saison d'opérations dans des conditions climatiques tempérées et moins humides du fait que la saison d'opérations ne soit pas suffisamment longue pour permettre à l'acclimatation et à la dégradation de s'opérer.

Des 16 HAP mesurés dans le cadre de cette étude, les huit énumérés ci-dessous ont toujours été décelés dans les sols de dépotoirs où les concentrations d'HAP étaient élevées par rapport aux niveaux ambiants: le phénanthrène, le fluoranthène, le pyrène, le chrysène, le benzo(a)pyrène, le benzo(a)anthracène, le dibenzo(a,h)anthracène et le benzo(g,h,i)pérylène. Dans les échantillons d'eau souterraine contenant de fortes concentrations d'HAP, l'anthracène et le chrysène étaient les composés les plus fréquemment identifiés, bien que des concentrations de phénanthrène, de fluoranthène, de pyrène, de benzo(a)anthracène, de benzo(a)pyrène, de dibenzo(a,h)anthracène et de benzo(g,h,i)pérylène ont été détectées dans les échantillons prélevés de certains sites.

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1 EXECUTIVE SUMMARY

Polynuclear aromatic hydrocarbons (PAH's) are chemicals which are found in oil refinery waste and are added to soil through application of refinery wastes on land, a practice commonly referred to as "landfarming". A program was initiated at the Wastewater Technology Centre (WTC) to investigate the fate and persistence of PAH's in soil in order to assess the possibility of environmental contamination arising from the practice of landfarming, and to assist in the development of technology to enhance the treatment of PAH's through land application of waste.

This report describes a study undertaken to collect information regarding the fate and persistence of PAH's in soil that had been previously treated with refinery wastes. The study is a sequel to a previous study concerning the fate and persistence of PAH added as pure compounds to previously untreated soil. It is intended to contribute to the current data base regarding the impact of PAH's in the environment and assist the development of recommendations for the land treatment of oily wastes.

The study was divided into three parts with the following objectives:

Part 1

1. To determine the persistence of PAH's in previously acclimated, waste treated soil under laboratory conditions, as assessed by conventional extraction and analysis for organic chemicals, and compare the results with those previously obtained for pure PAH's added to unacclimated soil.

2. To assess the effects of waste application levels on persistence of PAH's in oily waste applied to soil.

Part 2

1. To determine the persistence of PAH's in soil on existing land treatment field sites and compare the results with data obtained in laboratory studies.

2. To determine if concentrations of PAH's are elevated in groundwater beneath the land treatment field sites and if such contamination can be attributed to waste application.

Part 3

1. To identify the mechanisms involved in the disappearance of PAH's from previously acclimated, waste treated soil, using selected ^{14}C-labelled PAH's, and compare the results with those previously obtained for pure PAH's added to unacclimated soil.

2. To assess the effects of soil pH and nutrient addition on the treatment of PAH's in oily waste applied to soil.

Part 1 involved four soil treatments including control soil (never treated with waste) and refinery landfarm soil treated with waste at levels of 1%, 2% and 3% oil. The 2% oil treatment also received additions of chrysene

SOMMAIRE

Les hydrocarbures aromatiques polynucléaires (HAP) sont des composés chimiques qui se trouvent dans les résidus de raffinerie et qui sont additionnés au sol grâce à l'application des résidus de raffinerie au sol, pratique connue sous le nom "landfarming" (l'enfouissement par labourage des couches consécutives de résidus étendues sur le sol). Un programme fut amorcé au Centre technique des eaux usées (CTEU) dans le but d'étudier le devenir et la persistance des HAP dans le sol afin d'évaluer les possibilités de contamination du sol résultant de cette pratique et de venir en aide au développement de la technologie nécessaire pour améliorer le traitement des HAP au moyen de l'application des résidus au sol.

Ce rapport est une description d'une étude sur le devenir et la persistance des hydrocarbures aromatiques polynucléaires (HAP dans le sol traité antérieurement avec des résidus de raffinerie. L'étude donne suite à une étude antérieure concernant le devenir et la persistance des HAP additionnés sous forme de composés purs à du sol non traité antérieurement. Elle a pour but de faire une contribution à la banque de données existante en ce qui a trait aux impacts environnementaux des HAP et de faire un apport à l'élaboration de recommandations relatives au traitement dans le sol des déchets huileux.

L'étude était divisée en trois parties dont les objectifs étaient les suivants:

Partie un

1. Déterminer la persistance des HAP dans le sol antérieurement acclimaté et traité avec des résidus de raffinerie dans des conditions de laboratoire, selon une évaluation utilisant des méthodes classiques d'extraction et d'analyse de composés chimiques organiques, et comparer les résultats à ceux qui ont été obtenus antérieurement dans le cas de l'addition des HAP purs au sol non acclimaté.

2. Evaluer les effets des différents niveaux d'application de résidus sur la persistance des HAP dans les déchets huileux appliqués au sol.

Partie deux

1. Déterminer la persistance des HAP dans le sol à des sites de traitement par enfouissement dans le sol actuellement en exploitation et comparer ces résultats avec les résultats des études en laboratoire.

2. Déterminer s'il y a des concentrations élevées d'HAP dans l'eau souterraine dessous les sites de traitement par enfouissement dans le sol en exploitation et si de telles concentrations sont attribuables à l'application des résidus au sol.

Partie trois

1. Identifier les mécanismes impliqués dans la disparition des HAP du sol antérieurement acclimaté et traité avec des résidus de raffinerie, au moyen des HAP marqués au ^{14}C et comparer les résultats avec les résultats obtenus

and benzo(a)anthracene as pure chemicals. The treated soils were sampled periodically and analysed for oil and grease and a target list of 16 PAH's, as follows; naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b/k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene.

The ability of the research program to meet the objectives was severely limited by analytical variability, which included variable recovery of target chemicals for samples of the same soil/waste mixture. Variability in analysis was greater than the differences between treatments and therefore the effects of oil loading rates could not be assessed. In addition, loss of high molecular weight PAH from soil over the 200 days monitoring period was small and, given the high variability in analysis, could not be quantified. Where loss of PAH from soil was substantial, the results were generally similar to those observed using pure chemicals in the previous study. Loss of oil and grease from soil over the same period was substantial, indicating that hydrocarbon degrading organisms were present. There were no significant differences in rate of oil loss from soil with the three application levels.

Part 2 involved a field monitoring program in which soil and groundwater samples were taken from three operating landfarm sites over the period December, 1984 to October, 1985. The same analytical difficulties were encountered as described for the Part 1 study.

Loss of oil and grease on one of the field sites was similar to that which occurred in the laboratory study using the same soil (17% reduction from initial oil and grease level of 6% within 200 days). Losses from the three sites differed, however, with the highest proportion lost from the site with the lowest oil content (38% reduction from initial oil and grease level of 0.4%). Elevated PAH concentrations in soil and groundwater were associated with high oil and grease concentrations in soil. Nutrients were not added to soil at any site.

Loss of PAH's from field soil was similar to that observed in the laboratory study. As in the laboratory study, however, loss of the high molecular weight PAH's within 90 days could not be ascertained due to the high variability in the results. The results did suggest that there is the potential for high molecular weight PAH's to accumulate in soil under field conditions. Oil content in soil appeared to be related to the history of waste application at the sites, i.e. oil content was highest on the site with highest levels of previously applied waste. The PAH loading was also highest on the site with the greatest amount of oil. The relationship between oil and PAH content was not precise enough, however, to estimate loss of PAH's over a field season. Of the 16 PAH's measured in this study, the following 8 PAH's were consistently elevated in landfarm soils as compared to background levels; phenanthrene, fluoranthrene, pyrene, chrysene, benzo(a)pyrene, benzo(a)anthracene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene.

Concentrations of PAH's in groundwater near some landfarm sites were found to be elevated over background concentrations. On one site, however, the concentrations of PAH's in groundwater adjacent to a sewage trunk line, downstream from the landfarm, were greater than those observed near the

antérieurement dans le cas de l'addition des HAP purs additionnés au sol non acclimaté.

2. Evaluer les effets de l'addition de pH et de nutriments au sol sur le traitement des HAP qui se trouvent dans les déchets huileux appliqués au sol.

La partie un a comporté quatre différents traitements du sol y compris le sol témoin (c.-à-d. le sol n'ayant pas été traité avec des résidus) et le sol de dépotoir de raffinerie traité avec des concentrations d'huile de 1%, de 2% et de 3% respectivement. Le traitement à l'huile d'une concentration de 2% a également compris des additions de chrysène et de benzo(a)anthracène sous forme de composés chimiques purs. On a prélevé périodiquement des échantillons des sols traités dont on a analysé la teneur en huile et en graisse ainsi qu'en 16 HAP cibles, soit: le naphtalène, l'acénaphtylène, l'acénaphtène, le fluorène, le phénanthrène, l'anthracène, le fluoranthène, le pyrène, le chrysène, le benzo(a)anthracène, le benzo(b/k)fluoranthène, le benzo(a)pyrène, l'indeno(1,2,3-c,d)pyrène, le dibenzo(a,h)anthracène et le benzo(g,h,i)périylène.

La capacité de réaliser les objectifs du programme fut sévèrement limitée par la variabilité analytique, notamment la variabilité de la récupération des composés chimiques cibles à partir des échantillons prélevés d'un même mélange de sol et de résidus. La variabilité de l'analyse était plus prononcée que les différences entre les traitements et il était alors impossible d'évaluer les effets des différentes concentrations d'huile. En plus, le taux de disparition des HAP à poids moléculaire élevé dans le sol sur une période de suivi de 200 jours était très bas et, en raison de la grande variabilité de l'analyse, il était impossible de le quantifier. Lorsque la disparition des HAP était substantielle, les résultats étaient généralement semblables à ceux que l'on avait observé dans les cas des composés chimiques purs qui ont fait l'objet de l'étude précédente. Il y a eu une disparition substantielle d'huile et de graisse dans le sol durant la même période, ce qui indique la présence d'organismes qui décomposent les hydrocarbures. Il n'y avait aucun écart significatif entre les taux de disparition de l'huile dans le sol associés aux trois niveaux d'application.

La partie deux a consisté en un programme de suivi sur le terrain comportant le prélèvement d'échantillons de sol et d'eau souterraine aux sites de trois dépotoirs en exploitation sur la période allant de décembre 1984 à octobre 1985. On a rencontré les mêmes difficultés analytiques qu'on a éprouvé à la partie un de l'étude.

Le taux de disparition de l'huile et de la graisse observé à un des sites était semblable au taux enregistré par le même sol en laboratoire (une réduction de 17% sur une période de 200 jours de la concentration initiale d'huile et de graisse qui s'élevait à 6%). Le taux de disparition variait selon le site cependant, celui avec la plus faible teneur en huile enregistrant le taux le plus élevé (une réduction de 38% d'une concentration initiale de 0,4%). Les concentrations élevées d'HAP dans le sol et l'eau souterraine étaient associées aux concentrations élevées d'huile

landfarm operation. Anthracene and chrysene were most commonly measured at elevated concentrations, although concentrations of phenanthrene, fluoranthrene, pyrene, benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were also elevated at some sites. The environmental significance of PAH concentrations in groundwater associated with landfarming operations has not been assessed.

Part 3 involved detailed assessment of the fate of benzo(a)pyrene, naphthalene and anthracene in soil from a refinery landfarm site using additions of the chemicals labelled with ^{14}C radioisotope. Biologically active and sterilized soils with the ^{14}C-labelled chemicals were incubated in biometer flasks and subjected to two levels of pH and nutrient addition. This technique proved to be the most useful for identifying the loss of PAH's in soil, as there were fewer analytical difficulties (i.e. there was no interference with detection of the compound of interest) and the results were therefore more precise than in Parts 1 and 2.

In comparison with studies using unacclimated soil, it was observed that soil with a history of waste treatment was more effective in degrading the PAH's studied. Incorporation of carbon from the PAH molecule into microbial biomass also appeared to be more significant with the oil treated soil. The study confirmed that benzo(a)pyrene was degraded in soil, although an extensive acclimation period (80 days) was required. Substantial degradation of benzo(a)pyrene in a field situation may not be observed within one field season under temperate subhumid climatic conditions, however, as the effective length of the field season may be insufficient for both acclimation and degradation.

The techniques used to control soil pH in this study were not very successful and did not result in a satisfactory evaluation of the effects of pH on degradation. Nutrient addition did have a beneficial effect on overall microbial activity, but did not have a clear effect on PAH degradation.

This study contributes to the evaluation of refinery waste landfarming by providing information on the levels of PAH's in soil and groundwater associated with some landfarming operations and provides some insight into the fate of selected PAH's in waste treated soil. Limitations to the use of this data arise from the lack of precision obtained with current analytical methods and from the lack of environmental quality guidelines for PAH's with which to compare field observations. On the basis of observations made in this research program the following areas are recommended for future research:

1) Identification of concentrations of PAH's in soil and water which can be tolerated without detriment to health and the environment. Acceptable levels of PAH's may be dependent on soil type and other site-specific factors.

2) Improvement of routine methods of analysis for waste constituents in an oily matrix.

3) Identification of a) the period of time required to degrade high molecular weight PAH's under field conditions and b) site management methods which will increase the rates of degradation.

et de graisse dans le sol. On n'a ajouté des nutriments au sol à aucun des sites.

La disparition des HAP dans le sol en exploitation correspondait à ce qu'on avait observé dans le laboratoire. Cependant, comme dans le cas de l'étude en laboratoire, il était impossible de confirmer la disparition des HAP à poids moléculaire élevé sur une période de 90 jours en raison de la grande variabilité des résultats. Les résultats portent à croire, cependant, qu'il existe un potentiel d'accumulation des HAP à poids moléculaire élevé dans le sol dans des conditions d'exploitation. La teneur en huile du sol semblait se rapporter à la chronologie de l'application antérieure de résidus au site en question, c'est-à-dire que la teneur en huile était plus forte au site qui avait fait l'objet des niveaux les plus élevés d'application antérieure de résidus. La concentration d'HAP était également plus élevée au site ayant reçu la plus grande quantité d'huile. Le rapport entre la teneur en huile et la teneur en HAP n'était pas suffisamment précise, cependant, pour permettre d'estimer la disparition des HAP au cours d'une saison d'opérations. Des 16 HAP mesurés dans le cadre de cette étude, les huit qui suivent ont toujours été présents dans les sols de dépotoirs où les concentrations d'HAP étaient élevées par rapport aux niveaux ambiants: le phénanthrène, le fluoranthène, le pyrène, le chrysène, le benzo(a)pyrène, le benzo(a)anthracène, le dibenzo(a,h)anthracène et le benzo(g,h,i)pérylène.

Les concentrations d'HAP dans l'eau souterraine à proximité de certains sites de dépotoirs de raffinerie étaient élevées par rapport aux concentrations ambiantes. Dans le cas d'un site particulier, cependant, les concentrations d'HAP dans l'eau souterraine adjacente à un égout collecteur d'eaux vannes en aval du dépotoir étaient plus élevées que celles observées à proximité du dépotoir. Les concentrations d'anthracène et de chrysène étaient habituellement élevées, quoique les concentrations de phénanthrène, de fluoranthène, de pyrène, de benzo(a)anthracène, de benzo(a)pyrène, de dibenzo(a,h)anthracène et de benzo(g,h,i)pérylène ont été détectées dans les échantillons prélevés à certains sites. La signification environnementale des concentrations d'HAP dans l'eau souterraine associées aux opérations d'enfouissement par labourage n'a pas été évaluée.

La partie trois a comporté une étude détaillée du devenir du benzo(a)pyrène, du naphtalène et de l'anthracène au moyen de composés chimiques marqués au ^{14}C ajoutés à du sol prélevé d'un dépotoir de raffinerie. Des sols biologiquement actifs et stérilisés contenant des composés chimiques marqués au ^{14}C ont été incubés dans un flacon biomètre et traités avec deux différents niveaux de pH et de nutriments. Cette méthode s'est avérée la plus utile en ce qui a trait à la détermination de la disparition des HAP dans le sol du fait qu'elle comporte moins de difficultés analytiques (c.-à-d. que rien n'interférait avec la détection du composé visé) et qu'elle produit, en conséquence, des résultats plus précis que ceux obtenus dans les parties un et deux de l'étude.

Par comparaison aux études utilisant du sol non acclimaté, on a constaté que le sol avec une chronologie de traitement antérieur avec des résidus donnait de meilleurs résultats en ce qui concerne la dégradation

des HAP à l'étude. L'incorporation du carbone de la molécule d'HAP dans la biomasse microbienne semblait également être plus significative lorsque le sol était traité avec de l'huile. L'étude a confirmé que le benzo(a)pyrène se dégradait dans le sol, quoiqu'une période prolongée d'acclimatation (80 jours) était nécessaire. Il est possible qu'une dégradation substantielle du benzo(a)pyrène ne soit pas observée au cours d'une seule saison d'opérations dans des conditions climatiques tempérées et moins humides du fait que la saison d'opérations ne soit pas suffisamment longue pour permettre à l'acclimatation et à la dégradation de s'opérer.

Les méthodes utilisées dans le cadre de cette étude pour contrôler le pH du sol n'étaient pas très satisfaisantes et elles n'ont pas donné lieu à une évaluation satisfaisante des effets du pH sur la dégradation. L'addition de nutriments a eu un effet bénéfique sur l'activité microbienne mais n'a pas eu d'effet certain sur la dégradation des HAP.

Cette étude fait un apport à l'évaluation de l'enfouissement par labourage des résidus de raffinerie en fournissant des données sur les niveaux d'HAP dans le sol et dans l'eau souterraine associés à certaines opérations d'enfouissement et elle jette de la lumière sur le devenir de certains HAP dans le sol traité avec des résidus. Les limites à l'utilisation de ces données découlent du manque de précision éprouvé à l'égard des méthodes d'analyse en usage courant et de l'absence de lignes directrices sur la qualité environnementale relatives aux HAP auxquelles on pourrait comparer les observations sur le terrain. D'après les constatations de ce programme de recherche, il serait indiqué d'entreprendre des recherches supplémentaires dans les domaines suivants:

1) la détermination des concentrations d'HAP dans le sol et dans l'eau souterraine qu'on peut tolérer sans risquer de nuire à la santé ou à l'environnement. Les niveaux acceptables d'HAP pourraient varier selon le type de sol et d'autres facteurs spécifiques au site en cause;

2) l'amélioration des méthodes routinières utilisées pour analyser les constituants de résidus dans une matrice huileuse;

3) la détermination de a) la période requise pour la dégradation des HAP à poids moléculaire élevé dans des conditions d'exploitation et de b) les méthodes de gestion de site susceptibles d'accroître les rythmes de dégradation.

2 INTRODUCTION

Polynuclear aromatic hydrocarbons (PAH's) are chemicals which are found in oil refinery waste and are added to soil through application of refinery wastes on land, a practice commonly referred to as "landfarming". A program was initiated at the Wastewater Technology Centre (WTC) to investigate the fate and persistence of PAH's in soil in order to assess the possibility of environmental contamination arising from the practice of landfarming, and to assist in the development of operating practices to enhance the treatment of PAH's in the land application of waste.

In an initial study (Bulman et al., 1985) current literature was reviewed regarding the properties and sources of PAH's in the environment as well as processes affecting the persistence of PAH's in unacclimated soil with emphasis on microbial degradation of PAH's. In the initial study the kinetics were defined for disappearance of eight selected PAH's applied as pure chemicals to previously uncontaminated soil. Estimated first order half lives ranged from less than 12 days for naphthalene to 347 days for benzo(a)pyrene. Additional study of anthracene and benzo(a)pyrene, using ^{14}C-labelled, chemicals identified that volatilization and binding to soil solids as well as biological degradation were mechanisms responsible for decreasing concentrations of PAH's extracted from soil with time.

This report describes a study undertaken to collect similar information regarding the fate and persistence of PAH's in soil that has been previously treated with refinery waste. Analysis of the oily waste matrix is considerably less precise than that of pure chemicals in soil. By using soil from refinery land treatment sites, however, information was obtained for soils which have been acclimated to aromatic hydrocarbons for a number of years and which have much higher biological activity, overall, than the unacclimated soil. The effect of soil pH and nutrient addition on the fate of selected PAH's was studied to determine if liming or fertilizer addition may be used to enhance degradation of PAH's in soil. In addition, information was collected from land treatment sites which reflected the persistence of PAH's in land treatment soil under field conditions and the impact of land treatment on groundwater quality.

3 LITERATURE REVIEW

Microbial activity in oil treated soil has been the object of a great deal of study. The major emphasis has been on the degradation of oil, determination of suitable loading rates and amendments to enhance the rate of oil degradation. An API sludge, slop oil emulsion or tank bottom sludge may contain variable amounts of oil, ranging from 5 to 70% (PACE, 1980). Some studies have identified broad classes of chemicals in oily waste and reported on the distribution of these classes in soil with time. For example, it has been observed that as the concentration of oil in soil decreases through biodegradation, the concentration of aromatics, asphaltenes and resins increases (Cansfield and Racz, 1978; Ryan et al. 1986). Good general references on the degradation of oily waste in soil are found in Toogood (1977), Shilesky (1980), American Petroleum Institute (1983), Loehr et al. (1985) and Loehr and Malina (1986).

Determination of the concentrations of specific toxic trace chemicals, such as PAH's, has only recently received attention.

3.1 PAH Concentrations in Oil Refinery Waste

A major difficulty in studying specific organic chemicals in any complex waste is the identification of a suitable analytical protocol. Estimation of precision (via replicate analysis) and accuracy (via deuterated or surrogate chemical additions) is critical. Even for cases in which this information is good, interlaboratory comparisons have demonstrated that data may vary by as much as an order of magnitude. At present, reported concentrations can only be considered approximations. Comparisons of data from different studies must take these limitations into account. Relatively few reports have detailed PAH concentrations in an oily matrix.

A report by Burks et al. (1983) listed concentrations of specific organics in refinery wastewater streams and residues. In residues, 23 PAH's and substituted PAH's were detected, as summarized in Table 3.1.1. It should be noted that the concentrations of substituted PAH's greatly exceed those for unsubstituted PAH's. Many substituted PAH's are of substantial environmental importance due to toxic, carcinogenic and mutagenic properties. They were omitted from the current WTC study for simplification of analysis but they are worthy of future study in the assessment of land treatment practices.

The data in Table 3.1.1 (Burks et al., 1983) provides a comparison between the "fingerprint" of PAH's in refinery waste and that found in a light oil. A "fingerprint", in this context, refers to the types and relative concentrations of PAH's in a mixture. The light oil, in this case, contains fewer PAH's than the refinery waste and, not surprisingly, it is predominantly the high molecular weight PAH's which are missing.

Table 3.1.1 Concentrations of PAH's and substituted PAH's in refinery wastes, from Burks et al.(1983).

Compound	Concentration (mg/kg wet weight)			
	API Sludge	Slop oil Emulsion	DAF Float	Light oil
naphthalene	0.982	10.67	2.15	1.41
methyl naphthalene	7.824	65.06	17.21	4.29
dimethyl naphthalene	20.87	105.77	35.65	7.50
ethylnaphthalene	3.75	7.16	3.03	0.49
C_3 naphthalene	15.97	77.65	29.87	4.34
C_4 naphthalene	5.48	10.67	4.64	1.26
acenaphthene	<0.13	0.894	2.16	<0.20
fluorene	0.884	8.29	1.72	0.84
methyl fluorene	5.00	9.80	2.37	<0.20
C_3 fluorene	2.59	7.79	6.48	0.15
C_2 fluorene	0.713	3.46	3.87	<0.20
anthracene/ phenanthrene	23.40	34.04	41.48	0.38
ethyl anth/phen	90.66	77.06	145.90	1.45
C_2 anth/phen	107.10	56.91	150.10	0.65
C_3 anth/phen	37.12	14.75	27.99	0.21
C_4 anth/phen	12.43	<0.13	9.56	<0.20
pyrene/fluoranthene	61.76	10.93	67.66	<0.20
methyl pyr/fluor	<0.13	14.09	76.42	<0.20
C_2 pyr/fluor	39.53	3.38	41.98	<0.20
chrysene/ benzo(a)anthracene	97.56	9.99	101.30	<0.20
methyl chry/b(a)a	90.59	2.34	64.42	<0.20
benzo(a)pyrene/ benzofluoranthene	148.70	18.96	76.16	<0.20

A report by Streebin et al. (1984) listed, but did not quantify, organic compounds found in refinery land treatment soil. The list included anthracene, phenanthrene, fluoranthene, pyrene, naphthalene, chrysene, benzo(b)fluoranthene, benzo(a)anthracene, benzo(a)pyrene, dibenz(ah)-anthracene and benzo(g,h,i)perylene. Canviro (1983) reviewed literature for concentrations of trace constituents in oily wastes and reported preliminary results from a study by Can Test. The Can Test values and those reported in a similar review by Ryan (1986) (Table 3.1.2) are generally in agreement with the data of Burks et al. (1983). It is evident that PAH's are a class of organic chemicals which typically occur in refinery wastes in concentrations ranging from 1 to 150 mg/kg on a wet weight basis. Application of oily

sludges to dedicated land areas certainly results in the application of PAH's to soil and may result in accumulation of PAH's in soil with repeated applications.

Table 3.1.2 Concentrations of PAH's in refinery wastes, as reported in two literature surveys.

Compound	Concentration		
	Can Test (from Canviro, 1983)		from Ryan (1986)
	DAF Float (mg/kg wet)	API Sludge (mg/kg wet)	mixed waste (mg/kg wet)
acenaphthene	<87	ND	
acenaphthylene	<60	ND	
anthracene	ND	ND	
2-methyl anth	370	ND	
benzo(a)anthracene	ND	160	1 - 10
benzo(k)fluoranthene	ND	ND	
benzo(a)pyrene	ND	ND	1 - 10
chrysene	<51	140	1 - 10
fluoranthene	ND	ND	10 - 100
fluorene	<190	ND	
naphthalene	1430	ND	1,000 - 10,000
phenanthrene	1010	220	
pyrene	<17	120	

3.2 PAH Degradation in Oil Treated Soil

The degradation of specific PAH's in oily waste-treated soils has been studied by Bossert et al. (1985)in a 1280-day laboratory incubation. A series of 7 waste applications were made over a 920-day period, followed by an additional 360-day monitoring period. Substantial losses were observed as results of biotic and abiotic processes for PAH's with up to 4 rings. PAH's with 5 and 6 rings were persistent, however (Table 3.2.1).

Table 3.2.1 Losses of PAH's from soil treated with oily waste.

Compound name	Degradation			
	Bossert et al.(1984) 1280 days		Sims (1986) 90 days	
	total added (mg/kg)	loss (%)	total added (mg/kg)	loss (%)
fluorene	542	98.5	56	62
phenanthrene	1855	99.8	30	61
anthracene	389	93.1	38	89
fluoranthene	139	95.3	154	45
pyrene	286	14.4	177	58
benzo(a)anthracene	65.8	98.5	30	42
chrysene	55.3	96.9	27	59
benzo(b)fluoranthene	12.6	20.6	21	51
benzo(k)fluoranthene	77.0	70.1	14	38
benzo(a)pyrene	50.4	44.4	10	50
benzo(g,h,i)perylene	21.7	21.7	146	57
indeno(1,2,3-c,d)pyrene	----	----	9	68

Sims (1986) has summarized the results of several studies which identified degradation rates for PAH's in fossil fuel waste added to soil and explored the effects of enhancement techniques on degradation. Losses of PAH's in a single application of fossil fuel waste to unacclimated soil are presented in Table 3.2.1. As observed by Bossert et al. (1985), losses were generally greatest for PAH's with least rings.

Degradation of PAH's in an oily matrix was also studied by Energy Research and Technology (ERT, 1985) in creosote contaminated soil. Contaminant additions to soil were reported on the basis of benzene extractable hydrocarbons and ranged from 1.73% to 10.59% in soil. In a 4 month period, losses observed from soil were greater than 90% for 2 ring PAH's, greater than 80% for 3 ring PAH's and ranged from 0 to 60% for PAH's of 4 or more rings.

An extensive review of literature concerning loss of constituents of refinery waste in soil was prepared for the American Petroleum Institute (ERT, 1984). The results, however, were generally for pure PAH compounds added to soil, contaminated sediments, or for soil contaminated with creosote or wood preserving waste. Half-lives observed were for naphthalene (less than 30 days), substituted naphthalenes (3 to 23 days), phenanthrene (less than 30 days) and pyrene (54 and 99 days). Initial concentrations were not reported.

The results of these studies are generally in agreement. Substantial loss of 2 and 3 ring PAH's from refinery waste treated soil can be expected within a 3 to 4 month field season. Persistence in soil increases, however, with the number of rings in the molecule. Loss of PAH's with 4 or more rings may be substantial in a four month period. Loss rates are

variable, however, and may not be sufficient to ensure adequate treatment of refinery wastes through application to land.

Table 3.2.2 Comparison of half lives of PAH's in fossil fuel wastes with and without soil amendments (from Sims, 1986).

Compound	Half life (days)	
	without amendment	with manure and lime
fluorene	64	39
phenanthrene	69	23
anthracene	28	17
fluoranthene	104	29
pyrene	73	27
benzo(a)anthracene	123	52
chrysene	70	42
benzo(b)fluoranthene	85	65
benzo(k)fluoranthene	143	74
benzo(a)pyrene	91	69
benzo(g,h,i)perylene	74	42
dibenz(a,h)anthracene	179	70
indeno(1,2,3-c,d)pyrene	57	42

Sims (1986) reported that acclimation of soil resulted in higher loss rates than those observed in unacclimated soil. Degradation of benzo(a)pyrene was also shown to be stimulated by addition of phenanthrene, as a substrate analog, and by adjusting soil pH from 5.2 to 7.4. Loss of anthracene, phenanthrene and fluoranthene was greater from soil at 60 - 80% moisture, as compared to soil at 20 - 40% moisture. Half lives of PAH's in fossil fuel waste applied to soil were significantly reduced by amendments of manure and lime (pH adjustment of 6.1 to 7.5) (Table 3.2.2). Initial concentrations were as reported in Table 3.2.1.

The results indicate that there is potential for a high degree of degradation of PAH's, even in unacclimated soil. The evidence is clear that the degradation of target compounds in an oily waste applied to soil can be manipulated and should therefore be optimized by appropriate management techniques.

4 OBJECTIVES

The overall objective of the research program was to determine if PAH's in refinery waste are degraded through application to soil and to assess the potential for environmental contamination. The study is intended to contribute to the current data base regarding the impact of PAH's in the environment.

The study was divided into three parts with the following objectives:

Part 1

To determine the persistence of PAH's in previously acclimated, oil treated soil under laboratory conditions, as assessed by conventional extraction and analysis for organic chemicals, and compare the results with those previously obtained for pure PAH's added to unacclimated soil.

To assess the effects of waste application levels on persistence of PAH's in oily waste applied to soil.

Part 2

To determine the persistence of PAH's in soil on existing land treatment field sites and compare the results with data obtained in laboratory studies.

To determine if concentrations of PAH's are elevated in groundwater beneath selected operating land treatment sites and if such contamination can be attributed to waste application.

Part 3

To identify the mechanisms involved in the disappearance of PAH's from previously acclimated, oil treated soil, as assessed by selected ^{14}C-labelled PAH's, and compare the results with those previously obtained for pure PAH's added to unacclimated soil.

To assess the effects of soil pH and nutrient addition on the treatment of PAH's in oily waste applied to soil.

5 METHODOLOGY

5.1 Part 1 - Fingerprint Incubation

5.1.1 Experimental

Soil treatments were prepared from soil obtained from an oil refinery landfarm site (hereafter referred to as site C) which had received oily waste over a 10 year period and initially contained 7% oil. Four treatments were prepared, including control soil, 1%, 2% and 3% oil addition, with supplemental chrysene and benzo(a)anthracene added as pure chemical to the 2% oil treatment. Control soil was obtained from an area adjacent to the landfarm area, but which had not previously received oily waste. A 3720 g sample of landfarm soil was treated with 779 g waste (wet weight) containing 19.1% oil on a dry weight basis (3% oil addition to soil). Additions of benzo(a)anthracene and chrysene dissolved in 20 mL toluene were made to a 519 g sample of waste to achieve levels of 160 mg chrysene/kg and 140 mg benzo(a)anthracene/kg. The waste was then added to a 3981 g sample of landfarm soil (2% oil addition to soil). A 260 g sample of landfarm soil was treated with 4240 g waste (1% oil addition to soil). The four treatments were divided into triplicate samples of 1500 g each. Each replicate was incubated in an open ceramic pot under conditions excluding ultraviolet light within a research greenhouse. Moisture content was maintained at 25% dry weight (60% of water holding capacity). Temperature was allowed to vary seasonally between 20 and 30°C. Monthly sampling was performed with the soil being thoroughly mixed, 40 g being taken from each pot and analysed for PAH and oil and grease.

5.1.2 Analytical

For PAH analysis, an 8 g (wet weight) soil sample was extracted with acetone using a Polytron Homogenizer. The sample dry weight was determined on a separate aliquot. The acetone extract was transferred to a 2 L separatory funnel containing 1 L of purified distilled water. The 1 L sample was adjusted to pH 10 with NaOH, then extracted three times with distilled-in-glass hexane. The extracts were combined, evaporated and exchanged into 10 mL dichloromethane. For cleanup, a 5 mL aliquot was injected onto a gel permeation chromatography column containing 200 - 400 mesh S-X3 biobeads. The PAH fraction was collected and concentrated to 5 mL using a Rotovapor unit and exchanged into iso-octane. The sample was then applied to a prewashed 5 cm neutral aluminium oxide column. After an elution with 30 mL of 1% dichloromethane, the PAH fraction was eluted with 30 mL of 50% dichloromethane followed by 25 mL of benzene. The sample was concentrated and exchanged into dichloromethane for analysis.

Samples were analysed by Zenon Environmental Inc. by GC/MS on a Finnigan 4500 instrument. Details of analysis by Zenon, as described by the contract report, are reproduced in Appendix A.

For oil and grease analysis, a 15 g sample of soil was dried using $MgSO_4$ powder and ground to a fine powder by mortar and pestle. The sample was placed in a cellulose thimble for extraction with freon using a Labline multiunit extraction heater. The freon/oil mixture was separated using a Buchi Rotavapor unit and oil content was determined gravimetrically.

5.1.3 Statistical

The data was assessed qualitatively by comparing "fingerprints" for averages of triplicate analysis of the 14 PAH's in soil samples over time. Plots of the concentration of each PAH with time were compared for two of the four waste treatments.

For cases in which the plots indicated disappearance of at least 50% of the initial PAH, a first order kinetic model was fitted to the data. Half-lives and rate constants were computed and compared to those obtained in studies of pure chemicals (Bulman et al., 1985).

5.2 Part 2 - Landfarm Sampling

The sites to be included in the landfarm sampling program were selected with the assistance of the members of the PACE Environmental Quality Division Task Force. Criteria for selection were as follows:

a) landfarm currently in operation

b) groundwater sampling wells previously installed

c) gross parameter data available for previous years

d) within reasonable driving distance from the Wastewater Technology Centre (i.e. restricted to Southern Ontario)

Three candidate sites were identified and permission to conduct sampling was obtained. Representatives from PACE EQD Task Force and WTC met with each refinery Environmental Officer to obtain background information for the landfarm site and establish sampling procedures. The three sites are identified throughout the report as sites A, B and C.

5.2.1 Experimental

5.2.1.1 Soil Sampling

Soil samples were taken from each of the three refinery landfarm sites over a period of a year. At sites B and C the sampling was performed by WTC personnel, whereas at site A the sampling was performed by independent contractors. All sampling methods were kept as similar as possible.

Each field site was first blocked off according to a grid system with sample points randomly numbered. Site features and the soil and groundwater sample points are indicated in Figures 5.2.1.1a, b and c.

Site A was sampled according to the ongoing monitoring program at the refinery. Six areas were sampled with approximately twenty cores being taken from each area. Four of these areas (designated 1, 2, 3 and 4 in Figure 5.2.1.1a) received oily waste, previously and over the course of the study, and were considered replicates of oily waste treated soil. The remaining two areas (designated 5 and 6 in Figure 5.2.1.1a) received no oily waste and were considered control plots.

At site B, three replicate composite samples were prepared by taking five soil cores from each of four sample points, for a total of twenty cores per replicate. At site C, three replicate composite samples were prepared by taking four soil cores from each of five randomly located sample points, also for a total of twenty cores per replicate.

Site B consisted of two distinct regions, one of which supported vegetation and received no sludge over the course of the study. The samples taken from the vegetated area were composited into one replicate (designated replicate 3 in Figure 5.2.1.1b). For statistical purposes, then, the sampling design at site B was considered "blocked" rather than completely randomized.

Soil cores were taken by using a standard chromed steel core sampler. Topsoil samples (0-6" or 0-15 cm) were obtained at roughly one month intervals at all sites, while subsoil samples (6-12" or 15-30 cm) were taken twice at site A, in spring and fall, and on one occasion at site C. Each soil sample was placed in a 2 L borosilicate glass jar. The samples were prepared for analysis by homogenizing each replicate in a Hobart model stainless steel mixer and subsampling for PAH, oil and grease and metal content, as well as pH and conductivity analysis.

5.2.1.2 Groundwater Sampling

Groundwater samples were obtained with the aid of previously installed 3" diameter PVC plastic piezometers located on the perimeter of each landfarm field at all three sites. Personnel from WTC conducted the sampling at sites B and C, while independent contractors conducted sampling at site A. Piezometer sampling was conducted in two stages. Stage 1 involved pumping all standing water out of the piezometers and then allowing for an adequate groundwater recharge that usually occurred within a 36 - 48 hour period. Stage two involved the actual water sampling.

At sites B and C the following procedure was used for each piezometer pump-out. Piezometer caps were removed and initial water levels were measured using a Solinst water level detector. An IEA Aquarius model bladder-type pump with a battery powered control module, connected to a compressed gas air source, was then lowered into the piezometer until it was no less than 6" (15 cm) from the bottom. Groundwater was pumped out of the piezometer through a polyethylene tube and discharged at ground level. Pumping continued until all standing water had been discharged and then a second water level reading was recorded. The pump and tubing were then rinsed with distilled water, followed by methanol, followed by a second rinse with distilled water and wiped dry. The piezometer was recapped and the procedure repeated at the next piezometer.

For piezometer sampling it was imperative to obtain the best possible sample with a minimum of contamination and for this reason all water samples contacted only glass, stainless steel or teflon materials. The following procedure was used for all piezometer sampling at sites B and C. After an adequate recovery period following pump-out, the piezometer water level was measured and recorded. A teflon tube (0.9 cm diam., 0.3 cm wall thickness, 12 m length) was then inserted into the piezometer until it was 1' (30 cm) from the bottom. The tubing was then connected to a hand operated vacuum pump and a borosilicate jar via a stainless steel

attachment. Three litres of groundwater were sampled from each piezometer and then the tubing and other apparatus were rinsed with distilled water, methanol and distilled water again. The equipment was then wiped dry and used at the next piezometer.

As it was discovered that two piezometers at site C were substantially contaminated with diesel fuel, samples from these wells were always sampled last, to reduce the potential for cross contamination of samples.

At site A, each piezometer contained a dedicated pump and teflon tubing. Pumping of all standing water, with discharge at ground level, subsequent recovery and sampling of groundwater was performed in a manner similar to that at sites B and C.

Two litres of water were submitted for PAH analysis. The remaining liter was subsampled for oil and grease, dissolved organic carbon (DOC), pH and conductivity. For DOC analysis, subsamples were vacuum-filtered through 0.47 µm membrane filter paper. Samples contaminated with diesel fuel from site A were filtered through Celite, to remove the fuel, prior to DOC analysis.

5.2.2 Analytical

5.2.2.1 Analysis of Groundwater

The two 1 L borosilicate glass bottles collected on site were combined, homogenized and redivided in the laboratory to ensure that they would be analytical duplicates.

For PAH analysis, each 1 L sample was adjusted to pH 10 with NaOH, then extracted three times with distilled-in-glass hexane. The extracts were combined, evaporated and exchanged into an acetonitrile-water mixture for subsequent HPLC analysis.

Heavily contaminated samples were cleaned up by gel permeation chromatography prior to solvent exchange.

HPLC analysis was done on a reverse-phase ODS 5 µm column, solvent programmed from 50 to 100% acetonitrile. A dual detection system consisting of a U.V. (254 nm) and a fluorescence detector were used. In the latter part of the study a diode array detector was available to confirm the identity of the chromatographic peaks.

Samples for dissolved organic carbon analysis were filtered through a Sartorius 0.45 µm filter membrane. Analysis was performed using a Dohrmann DC-80 total carbon analyser system. The system converts carbon to CO_2 by UV promoted oxidation and measures CO_2 using a non-dispersive IR detector.

5.2.2.2 Analysis of Landfarm soils.

For PAH analysis, an 8 g (wet weight) soil sample was extracted with acetone using a Polytron Homogenizer. The sample dry weight was determined on a separate aliquot. The acetone extract was transferred to a 2 L separatory

funnel containing 1 L of purified distilled water and the sample then treated as described above for liquid samples.

The extracts were sent to Zenon Environmental Inc. for cleanup and analysis. The extracts were purified by gel permeation on a Bio-Beads SX-3 column. The samples were then analysed by GC-MS on a Finnigan 4500 instrument. Details of the analysis performed by Zenon, as described in the contract report, are reproduced in Appendix A.

Oil and grease analysis were performed as described in section 5.1.2.

Soil pH and conductivity measurements were performed using a 25.0 g soil sample in 50 mL deionized water.

For total Ca, Cd, K, Mg, Na, Pb and Zn analyses, an aqua regia digestion was performed as follows. A 0.5 g of dry pulverized (300 mesh size) soil sample was placed in a 250 mL TFE beaker and the sides of the beaker were rinsed with 10 mL distilled water. Added to this were 100 mL of nitric acid. The beaker was covered and placed on a hot plate at 200-250 C and the solution was evaporated to near dryness. After cooling (5 minutes), 10.0 mL of concentrated hydrochloric acid followed by 30.0 mL of concentrated nitric acid, approximately 3.0 mL of 30% hydrogen peroxide and lastly, 50.0 mL of distilled water were added. The covered beaker was once again placed on the hot plate and the solution was evaporated to dryness. After cooling, 3.0 mL of concentrated nitric acid, 10.0 mL of concentrated hydrochloric acid, approximately 3.0 mL of hydrogen peroxide, 10.0 mL of concentrated hydrofluoric acid and 30-50 mL of distilled water were added. Once again the solution was evaporated to dryness on the hotplate. If any gritty material was still present then 20.0 mL of concentrated nitric acid, 5.0 mL of concentrated hydrofluoric acid, 3.0 mL of 30% hydrogen peroxide and 20.0 mL of distilled water were added and again this solution was evaporated to dryness. Finally, 10.0 mL of concentrated hydrochloric acid, 3.0 mL of concentrated nitric acid, approximately 3.0 mL of 30% hydrogen peroxide and approximately 50.0 mL of distilled water were added and the uncovered beaker was heated on the hotplate. The solution was evaporated to approximately 15.0 mL, cooled, diluted to 25.0 mL with distilled water and transferred to a plastic bottle.

For Cr analysis, a lithium metaborate fusion technique was used. A 0.2 g of sample was weighed into a porcelain crucible and 1.4 g of lithium metaborate flux were added. The mixture was transferred to a graphite crucible and placed in a preheated muffle furnace for 15 minutes at 900 C. The crucible contents were then placed into a 100 mL pyrex beaker and mixed with 80.0 mL of 4% nitric acid. The solution was stirred and then transferred to a 200 mL volumetric flask and made up to volume with 4% nitric acid.

Atomic absorption analysis was performed on the final sample solutions with a Perkin Elmer model 403 or 503 Atomic Absorption Spectrophotometer.

5.2.3 Statistical

5.2.3.1 Groundwater

The two dimensional spatial distributions of each of the 15 PAH analysed in

groundwater were assessed for each land treatment site by superimposing concentration data on the appropriate site plan. This data was further assessed qualitatively by comparing fingerprints of PAH concentrations in groundwater with those in the treated soil and, in the case of Site C, wells contaminated with diesel fuel and oil.

5.2.3.2 Soil

The data was assessed qualitatively by comparing fingerprints for averages of triplicate analysis of the 14 PAH's in soil samples over time. Plots of the concentration of each PAH with time were compared for each site.

5.3 Part 3 - Incubations with ^{14}C-labelled PAH's

5.3.1 Experimental

Soil taken from land treatment Site C was put through a No. 10 mesh (2 mm) sieve and brought to 25% moisture (dry weight). Soil characteristics were as described in Part 1.

For each incubation study, three soil treatments were prepared ($HgCl_2$ addition, pH and nutrient addition) with two levels of each treatment and replicated three times (replicated 2^3 factorial design). In addition, triplicate control flasks were prepared with and without $HgCl_2$.

The treatments were prepared as follows. A 480 g sample of soil was divided into two 240 g portions, one of which was treated with the low level of nutrient addition (600 mg/kg N, 60 mg/kg P), and one which was treated with the high level of nutrient addition (1000 mg/kg N, 100 mg/kg P). One half of each portion was further treated with 2% (w/w) $HgCl_2$ to inhibit microbial activity while the other remained biologically active. These samples were then divided into two 60 g portions, one of which received drops of H_2SO_4 delivered from a disposable Pasteur pipette to reduce the pH to 4.5. Control soil was prepared by treating one of two 60 g aliquots of soil with $HgCl_2$ and adding the low level of nutrients to both. Each treatment thus consisted of 60 g soil.

The treatments were divided into triplicate 20 g soil samples and placed in Bellco biometer flasks, illustrated in Figure 5.3.1 and described by Bulman et al. (1985). A total of 24 flasks was prepared for each incubation. For the incubation with benzo(a)pyrene, a polyurethane foam plug was inserted between the main flask and the reservoir for collection of organic volatile compounds. In the anthracene and naphthalene incubations, volatile emissions were trapped by attaching a florisil column to the syringe during aeration. The column was made of an inverted, disposable, pasteur pipette packed with florisil between glass wool. The pipette was fixed to the syringe with a 1.5 cm length of viton tubing.

The PAH addition was made to all but control soil by pipetting either 7,10-^{14}C benzo(a)pyrene (2.63×10^7 disintegrations per minute), 9-^{14}C anthracene (1.30×10^7 dpm) or 1-^{14}C naphthalene (1.16×10^7 dpm) in 1, 1, and 0.5 mL toluene, respectively. The flasks were sealed with stoppers

wrapped in aluminum foil and teflon tape and were stored in a Precision Scientific Incubator at 20°C.

The incubation with benzo(a)pyrene proceeded for 92 days, with anthracene for 116 days and with naphthalene for 65 days. The flasks were aerated twice weekly by injecting 200 mL air through the ascarite filter. Sampling of the florisil columns and NaOH was performed weekly. Triplicate blank flasks were prepared exactly as the treatment flasks, but without soil samples.

5.3.2 Analytical

The ^{14}C was originally applied to the biometer flask soil as a labelled PAH. After incubation, the ^{14}C atom could have existed as part of the parent compound or incorporated into a degradation product. Both parent compound and degradation products could have been associated with the soil matrix, incorporated into biomass or volatilized. The ultimate degradation product in an aerobic system is CO_2, but intermediate degradation products may also be present. The PAH's used in this study were not uniformly labelled. Rather, they were labelled in specific locations with ^{14}C. As degradation proceeded, the ^{14}C could have been removed with small fragments of the parent PAH, or remained with the rest of the molecule.

^{14}C was quantified in the following matrices:

NaOH Absorbent Solution
Florisil Adsorbent Trap (naphthalene and anthracene only)
Polyurethane Adsorbent Plug (benzo(a)pyrene only)
Soil (Extractable)
Soil (Non-extractable)

Volatile ^{14}C was further characterized as being organic or inorganic, polar or non-polar. The ^{14}C extracted from soil was characterized as being polar or non-polar, and, in the latter stage of the project, identified as parent compound or as degradation product by HPLC. The parent PAH is extractable and is non-polar. The ^{14}C found in any other fraction can be interpreted as a degradation product.

5.3.2.1 Materials

All ^{14}C-labelled chemicals used as tracers were obtained from California Bionuclear Corp, Los Angeles, California. Naphthalene (1-^{14}C), Anthracene (9-^{14}C) and Benzo(a)pyrene (7,10-^{14}C) were purchased at 98% minimum radiochemical purity and were used as received. They were analysed by silica gel column chromatography to ensure the absence of oxidation products. The labelled compounds were dissolved in toluene for application to the biometer flask soil.

All samples were counted for ^{14}C on an LKB model 1217 Liquid Scintillation Counter. The External Standard Ratio (ESR) method of automatic window setting and the ESR method of quench correction for dpm calculation was used. Chemiluminescence was routinely monitored by the instrument and was negligible.

The HPLC was carried out using a Waters HPLC system with a Berthold 505 of

two model 501 solvent delivery systems, a model 680 gradient controller, an in-line filter, a u-Bondapak C-18 guard column, and a u-Bondapak C-18 analytical column (3.9 mm x 30 cm). The Radioactivity Monitor was operated in ^{14}C mode with a 0.15 mL "H" cell (a solid scintillator cell). The analogue output from the Radioactivity Monitor was integrated using a Waters 740 Data Module. The mobile phase was 60:40 water:methanol held isocratic for 5 minutes, then increased linearly to 100% methanol over 30 minutes.

Combustion analysis of the samples was carried out in an R.J. Harvey Biological Material Oxidizer (BMO).

All samples were counted in 22 mL plastic vials with 10 mL of Scintiverse II scintillation cocktail (Fisher Scientific). Standards were prepared by dissolving one LKB-Wallac ^{14}C Internal Standard pellet (^{14}C = 105400 dpm) in 10 mL of scintillation cocktail and adding various volumes of blank sample to the mixture. Several standards formed the quench calibration curve and were stored in the instrument memory for automatic dpm calculation. Reagents used were DIG acetone, methanol, toluene, hexane, isooctane, 2-propanol (Caledon Laboratories), reagent grade NaOH, acetic acid (Fisher Scientific), mannitol (BDH). The CO_2 trapping solution for the BMO was Carbo-sorb (United Technologies Packard) mixed 1:2 with Scintiverse II.

All columns for vapour phase adsorption and for column chromatography were prepared in large volume pasteur pipettes. These pipettes (9 mm id, 15 cm long) were packed with about 4 cm^3 of adsorbent material sandwiched between plugs of glass wool. The vapour phase adsorbent was Florisil (60-100 Mesh, EM Science). The column chromatography adsorbent was Silica Gel (100-200 Mesh, Woelm Pharma).

5.3.2.2 Methods

Degradation of ^{14}C-labelled organic chemicals was detected by trapping and analysis of liberated $^{14}CO_2$. Radioactive and "cold" CO_2 as well as other volatile compounds were trapped in 2M NaOH. Total ^{14}C was obtained by direct counting of a 1 mL sample of NaOH. A second 1 mL portion of NaOH was extracted with 4 mL of hexane by shaking in a test tube, and the hexane and extracted NaOH separated and counted. Any non-polar organic compound such as volatilized PAH will extract into the hexane, but dissolved carbonate remains in the NaOH. The NaOH was neutralized with an equal volume of 2M acetic acid before counting.

When the biometer flasks containing ^{14}C-naphthalene or anthracene were aerated, the 200 mL of air displaced was passed through a column packed with florisil to trap any volatile organic material. Elution with different solvents caused separation of non-polar and polar chemicals for ^{14}C counting. Non-polar compounds were first eluted with two successive 5 mL portions of toluene; polar compounds were then eluted with two successive 5 mL portions of methanol. Two successive 5 mL portions of solvent were used to make certain that most of the activity was eluted in the first portion. This procedure confirmed that good chromatographic elution has taken place. The count rates of the two solvent portions were added.

Flasks containing ^{14}C-benzo(a)pyrene were fitted with a polyurethane plug which remained in place throughout the incubation period. At the end of the incubation, the entire polyurethane plug was extracted overnight in a soxhlet apparatus using 300 mL of 1:1 Hexane:Acetone. The extract was evaporated to 15 mL on a rotary evaporator. A 1 mL sample of the concentrate was taken for counting.

At the end of the incubation a 5 gram soil sample from each biometer flask was extracted overnight in a soxhlet apparatus using 300 mL of 1:1 Hexane:Acetone. Three mL of iso-octane was added and the extract evaporated to about 10 mL on a rotary evaporator. An additional 50 mL of hexane was added and the volume reduced to 10 mL in order to remove the last traces of acetone. The sample concentrate was then made up to 15 mL. A 0.1 mL sample of the concentrate was taken for counting and another 0.1 mL sample of the concentrate was chromatographically separated into parent and metabolite. In the benzo(a)pyrene and naphthalene studies a 0.1 mL sample was added to the top of a silica gel column. The column was eluted with two 5 mL portions of hexane, followed by two 5 mL portions of toluene, followed by two 5 mL portions of methanol. Non-polar material (PAH) was eluted with toluene, while polar material (degradation products) eluted with methanol. The initial hexane elution was to ensure that all the radioactivity was first sorbed to the silica gel. In the anthracene study the concentrate was analysed by HPLC.

After air drying to remove solvent, samples of extracted soil and extracted polyurethane plug (0.05 - 0.1 gram) were combusted in a stream of oxygen at 900°C in a Biological Material Oxidizer. After catalytic oxidation of combustion gasses, the resulting CO_2 was trapped for counting.

5.3.3 Statistical

Each incubation study was designed as a replicated 2^3 factorial experiment. The distribution of ^{14}C among components of the soil and atmosphere in the flasks was assessed by construction of a mass balance table. Treatment effects (sterilization, fertilizer addition and pH) were assessed by analysis of variance. The rate of mineralization to ^{14}C-labelled CO_2 was assessed by regression analysis with a first order kinetic model.

FIGURE 5.2.1.1a SITE A LANDFARM MAP

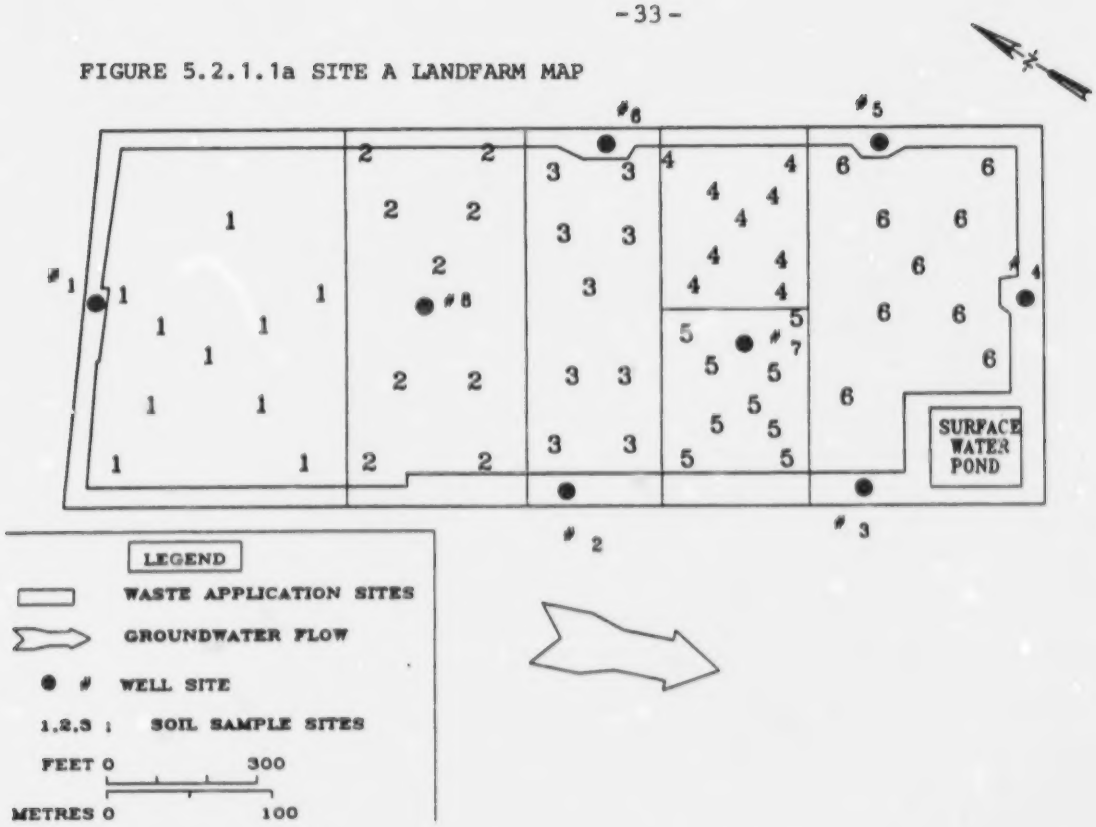


FIGURE 5.2.1.1b SITE B LANDFARM MAP

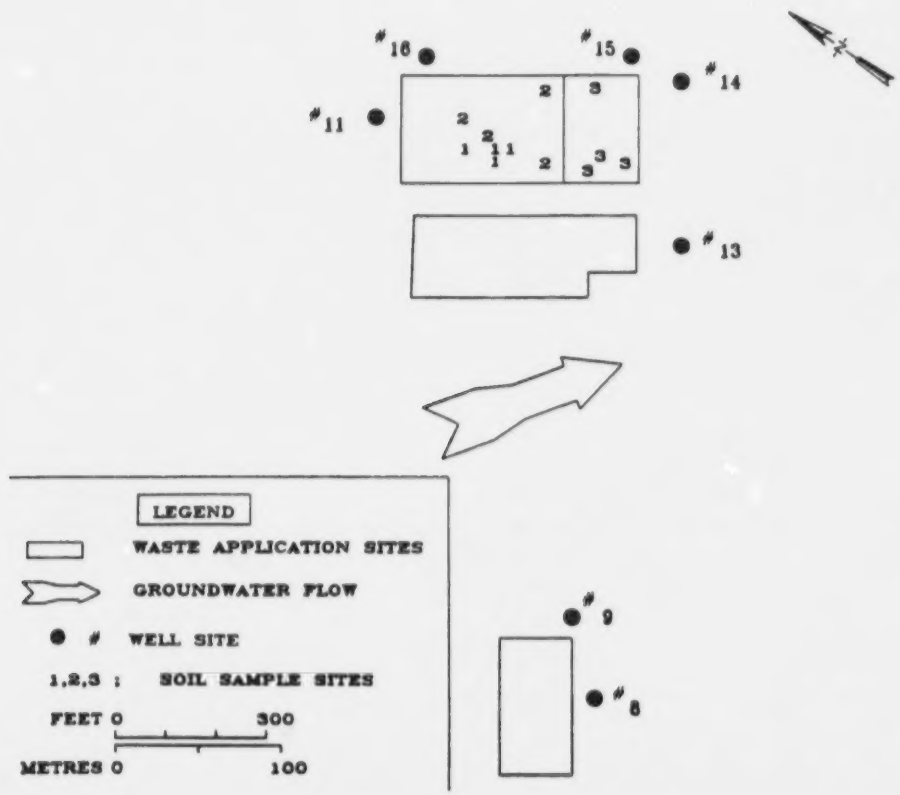
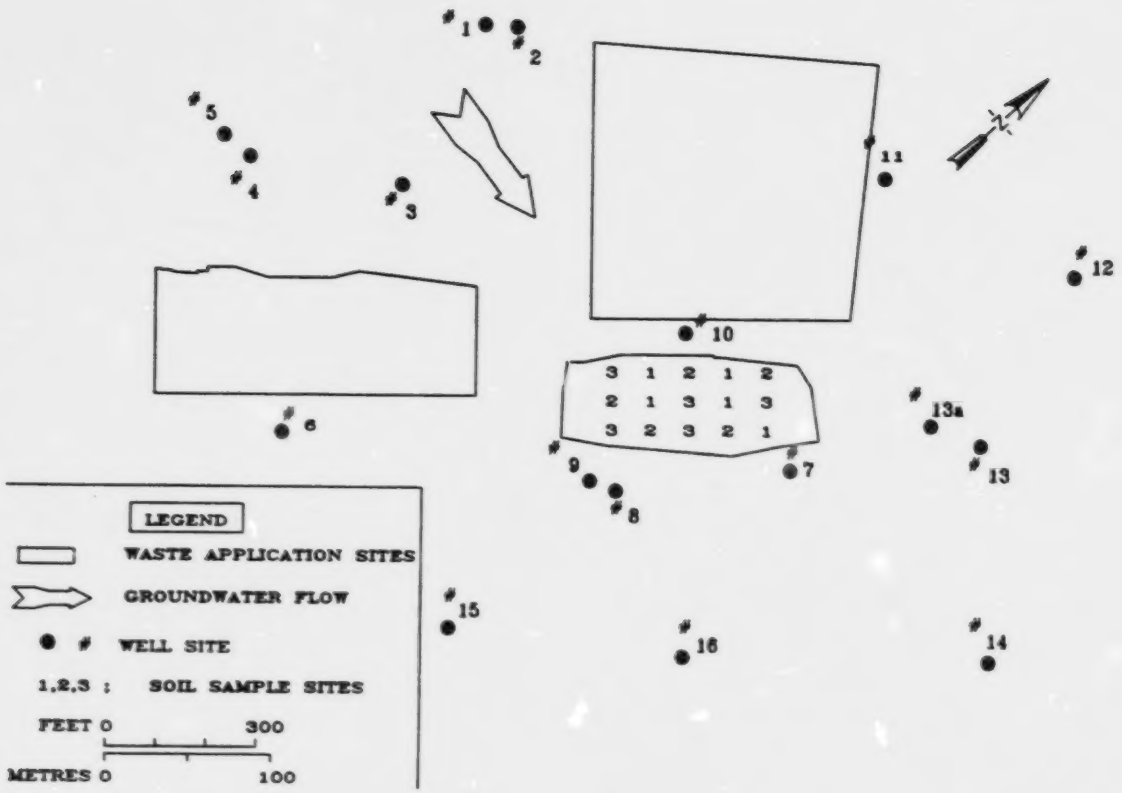


FIGURE 5.2.1.1c SITE C LANDFARM MAP



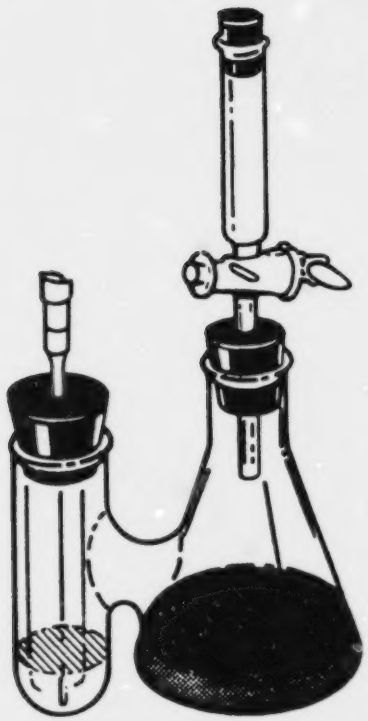


FIGURE 5.3.1 BIOMETER FLASK USED IN SOIL INCUBATIONS WITH ^{14}C.

6 RESULTS AND DISCUSSION

6.1 Part 1 - Kinetic Incubation Study

6.1.1 Persistence of Target Chemicals in Soil

The Part 1 study involved laboratory incubation of refinery waste in soil in order to assess the kinetics of PAH loss from soil. Results are presented for the concentration of oil and grease and 16 target PAH's in soil with three oily waste treatments (addition of 1%, 2% and 3% oil). The total incubation period was 483 days. A complete set of data is presented for oil and grease results, but results for individual PAH's are only available for a 234 day period and for two of the three waste treatments. Although the two treatments which were monitored for PAH concentration differed in waste application, the differences in additions of target PAH constituents proved to be less than sample variability. The PAH results for the two treatments are therefore presented together.

The PAH data are extremely variable, as one might expect with a heterogeneous mixture of oily waste and soil. For several compounds there appear to be decreasing trends in concentration with time. Care must be taken in interpreting this data, however, as the recovery of target chemicals was also extremely variable both between sample periods and between chemicals. To assist in interpretation of results, the data was compared to analytical recovery and to previous results obtained from pure chemicals incubated with soil.

To confirm trends observed in the data, the results of spiked duplicate samples were used to calculate recovery of target chemicals from the same sample and adjust the sample concentration accordingly. Three spiked duplicate samples for the 2% oil treatment, covering the initial and two final sample periods, were available for this confirmation (presented in Appendix B). Use of this technique was intended only to assist in interpretation of the data, not to produce a more reliable or conclusive data set.

Several chemicals were detected only in the initial sample period, and data for those chemicals is presented in tabular form (Table 6.1.1). For the remainder of the chemicals, data is presented against a logarithmic scale for concentration to facilitate estimation of first order kinetic parameters. This method of illustration also provides a simple method for comparison with data collected using pure chemicals in soil (Bulman et al., 1985). The detection limits for all PAH's in soil were 0.2 mg/kg. Not detected data are represented graphically along the x-axis (log concentration of -2). First order half lives have been estimated, with 95% confidence limits, for loss of a chemical only if the loss was confirmed by spiked duplicate samples. Kinetic parameters were estimated strictly for descriptive purposes and do not imply that conclusions should be based on this data. Detailed kinetic modelling of the data was not performed due to the high variability in the data.

Table 6.1.1 Concentrations in soil of PAH's detected only in initial samples (three replicate samples).

	Sample		
	A	B	C
Naphthalene	1.0	nd	1.4
Acenaphthylene	.51	nd	.22
Acenaphthene	.26	nd	.69
Fluorene	.28	nd	.71

The PAH's detected only in initial samples were of low molecular weight and, relative to the other PAH's, high water solubility and volatility. Recovery of all four PAH's from oil treated soil was poor, 6-7% for the initial period (Appendix B). Recoveries of naphthalene, acenaphthylene and acenaphthene from oil treated soil in the last two periods, was 0%. Without additional recovery data from oil treated soil in earlier sample periods, it cannot be concluded that these PAH's were actually lost from soil. Based on the physical parameters of these PAH, however, it is speculated that loss from soil did, in fact, take place. The volatility of these chemicals may have contributed to low analytical recovery. Loss from soil appeared to occur within the first 24 day period. These results were consistent with results observed for pure naphthalene added to soil (Bulman et al., 1985).

Phenanthrene was detected throughout the incubation period, however the concentration appeared to drop within the first 25 day period and was not detected in all samples. Detected values are plotted against a log scale for concentration in Figure 6.1.1. Recovery of phenanthrene was poor for the initial sample period but improved in the second last period (Appendix B), suggesting that the observed decrease in concentration was not the result of poorer recovery but was due to loss from soil. Approximate concentrations of phenanthrene, adjusted for analytical recovery, were 9.4 mg/kg initially and not detected after 206 days. A first order curve fitted to the data for the first two sample periods (R^2=0.5098) resulted in a rate constant of -0.0474 (+/-84%). This predicts a first order half-life of 15 days which is consistent with observations of pure phenanthrene in soil (Bulman et al., 1985).

Anthracene was not detected in the oil treated soil, although analytical recovery of anthracene was similar to that of phenanthrene (Appendix B).

Pyrene data is presented in Figure 6.1.2 using a logarithmic scale for concentration. The concentration of pyrene appeared to decrease over the 234 day incubation period. In contrast, although the analytical recovery of pyrene was poor initially, it increased for the 206 and 234 day sample periods (Appendix B). Approximate concentrations of pyrene, adjusted for analytical recovery, decreased from 59.9 mg/kg initially to 24 mg/kg after 206 days and 2 mg/kg after 234 days, confirming loss of pyrene from soil. Due to poor recovery, the initial sample period was omitted from curve fitting. A first order curve fit the data from 24 to 234 days (R^2=0.3771) with a rate constant of -0.0072 (+/-54%) for a half life of 120 days

(including the initial 24 days). First order kinetics imply that the rate of loss of pyrene would decrease with time. Concentrations adjusted for analytical recovery, however, suggested an accelerated decrease in concentration over the 206 to 234 day period and that there may have been an initial period of acclimation (approximately 200 days) or that the rate of loss of pyrene from soil was other than first order. In studies with pure pyrene added to soil, an acclimation period of 26 days was observed followed by loss with first order kinetics for a half life of 58 days.

Chrysene data is presented in Figure 6.1.3. The data is extremely variable and no trend with time is evident. Recovery of chrysene in spiked duplicates was poor for the initial sample period and nil for the last two periods (Appendix B), although chrysene was detected in non-spiked samples. In studies with pure chrysene in soil it was observed that no significant loss from soil occurred over a period of 400 days (Bulman et al., 1985).

Benzo(a)anthracene was detected in oil treated soil in the second and third monitoring period only. Detected values, illustrated in Figure 6.1.4., do not demonstrate a trend. Lack of detectable benzo(a)anthracene in the initial and final periods can be explained by lack of analytical recovery (Appendix B). Benzo(a)anthracene was not detected in the second to last period, however, when recovery was very good. The results suggest that benzo(a)anthracene was lost from soil within the 59 to 206 day period. In studies with pure benzo(a)anthracene in soil, loss from soil occurred after a period of 40 days with a half life of over 100 days (Bulman et al., 1985).

Fluoranthene was not detected in oil treated soil, although analytical recovery was similar to that of benzo(a)anthracene (Appendix B).

Benzo(b)fluoranthene and benzo(k)fluoranthene could not be analytically resolved and the concentrations illustrated in Figure 6.1.5 represent the chromatographic peak area of both chemicals. With the exception of the initial concentration, there appears to be a trend towards decreasing concentration over time. The data is extremely variable, however. Recovery from spiked samples was poor for the initial and second to last period and nil for the last period (Appendix B). Based on the poorer recovery observed in later sample periods, it could not be concluded that these chemicals were lost from soil over the incubation period.

The concentrations of benzo(a)pyrene are presented in Figure 6.1.6. The data was extremely variable and no trend with time was observed. Analytical recovery was also variable; poor for the initial sample period, nil for the second to last period and high for the final period (Appendix B). Although concentrations for the first and last period, adjusted for analytical recovery, indicated a decrease from 23 mg/kg to 4 mg/kg in 234 days, the variability between samples (as indicated by a recovery of benzo(a)pyrene greater than 100% for the last period) was such that this may not have been a reliable estimate of loss of benzo(a)pyrene in the soil. Observations of pure benzo(a)pyrene in soil demonstrated no loss over a period of 400 days (Bulman et al., 1985).

The results for dibenzo(a,h)anthracene are presented in Figure 6.1.7. With the exception of data from the initial period, there appears to be a decreasing trend in concentration with time. Analytical recovery for these

samples was, however, consistently poor for the initial and final two sample periods (Appendix B). Although the concentration of dibenzo(a,h)anthracene decreased below detection after 234 days in one sample, other samples contained similar concentrations initially and after 206 and 234 days, therefore loss of dibenzo(a,h)anthracene from the soil was not positively confirmed.

Indeno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene were similar in that their concentrations were extremely variable and showed no trend with time (Figures 6.1.8.and 6.1.9) and their analytical recovery was poor and also variable (Appendix B). Both chemicals were detected in samples after 234 days at concentrations similar to those observed initially. The results suggest that neither chemical was lost from soil to an appreciable degree over the 234 day period.

The results of oil and grease monitoring over the 483 day incubation period are presented in Figure 6.1.10. Although some variability was observed in the data, it was low enough to be able to distinguish between the waste treatments. Loss of oil from soil proceeded immediately and appeared to be linear over most of the incubation (0 to 416 days), however the rate of loss appeared to decrease toward the end of the incubation as the concentrations approached 6%. The results showed a modest decrease in oil and grease content (17% of initial concentration) within a 120 day period (equivalent to one landfarm field season). Nutrients were supplied to the soil throughout the incubation in solution form. It is therefore unlikely that oil degradation was inhibited by lack of nutrients. It is most likely that the remaining 6% of oil in soil was composed of less readily degradable material and less volatile material, so that loss from soil proceeded more slowly. A linear model was fitted to data over the 416 day period. Rates of -0.0071 (+/-0.0013; R^2=0.9067), -0.0091 (+/-0.0014; R^2=0.9434) and -0.010 (+/-0.0004; R^2=0.9790) were observed for the 1%, 2% and 3% treatments, respectively. The rate constants were not significantly different between treatments. The results confirm that substantial degradation of hydrocarbon occurred over the incubation period at similar rates for all three treatments.

6.1.2 Discussion of Kinetic Study Results

The intent of the kinetic study was to provide enough information on loss of PAH's from oily waste treated soil for comparison with detailed kinetic information obtained with pure chemicals added to soil (Bulman et al., 1985), recognizing that analytical precision would be sacrificed with oily waste treated samples. As anticipated, sample variability and analytical variability were encountered which severely limited the conclusions that could be drawn from the data. The degree of variability in analytical recovery among samples, however, had not been anticipated. Calculation of concentration based on a measured value combined with analytical recovery does not necessarily provide a better estimate of the concentration of a chemical in a sample. It was useful in this study, however, as a check on the trends in data, i.e. to identify if a decreasing trend could be attributed to poor recovery or to loss from soil.

Many of the PAH's identified in the oil treated soil had been previously studied as pure chemicals in soil (Bulman et al., 1985) and, in general, the two studies produced similar results. The low molecular weight PAH's

disappeared quickly from the soil, whereas the high molecular weight PAH's appeared to be persistent over a 200 day incubation period. In the case of phenanthrene, the rate of loss from oil treated soil appeared to be similar to that from soil treated with pure chemical. Pyrene appeared to be more persistent in the oil treated soil, whereas benzo(a)anthracene appeared to be less persistent. Data for chrysene and benzo(a)pyrene were too variable to be conclusive. No evaluation could be made of the effect of sludge application level or pure chemical addition in this study, as the differences between treatments were less than the analytical variability.

Monitoring of total oil and grease concentration suggested that an active hydrocarbon degrading population existed in the soil. Some loss of oil would likely have occurred through volatilization, however, this was not measured. Oil application level had no apparent effect on oil degradation rates over the range of concentrations in this study.

In comparison with Sim's data (1986) for unamended soil, the low molecular weight chemicals in this study were lost from soil more rapidly, possibly because the soil organisms were acclimated. The high molecular weight chemicals, however, were more persistent in this study than as reported by Sim's. As observed in the study using pure chemicals (Bulman et al., 1985), a rapid loss of chemical from soil is easily determined, whereas a gradual loss of chemical from soil is difficult to quantitate if there is substantial variability in the data. It is possible that loss of high molecular weight PAH from oil treated soil did occur within 200 days in this study, but was less than the observed sample variability. Increased precision in monitoring these chemicals in an oily matrix is required if accurate estimates of degradation rates in oil treated soil are to be made. From the results of this study, it would appear that a major limitation in obtaining the desired precision is in the recovery of chemicals as they are extracted from soil and carried through the intensive cleanup procedure.

FIGURE 6.1.1 CONCENTRATION OF PHENANTHRENE IN WASTE TREATED SOIL

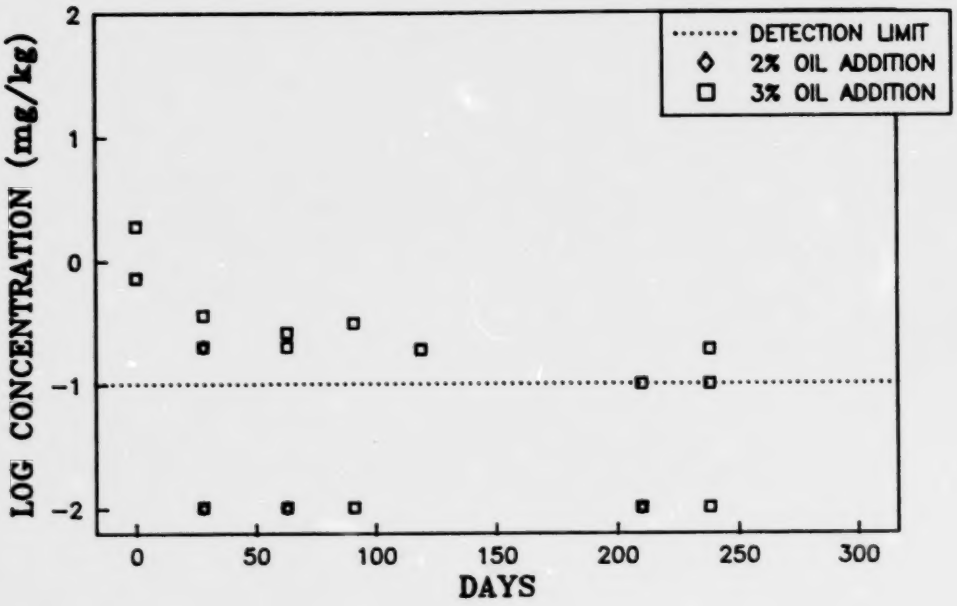


FIGURE 6.1.2 CONCENTRATION OF PYRENE IN WASTE TREATED SOIL

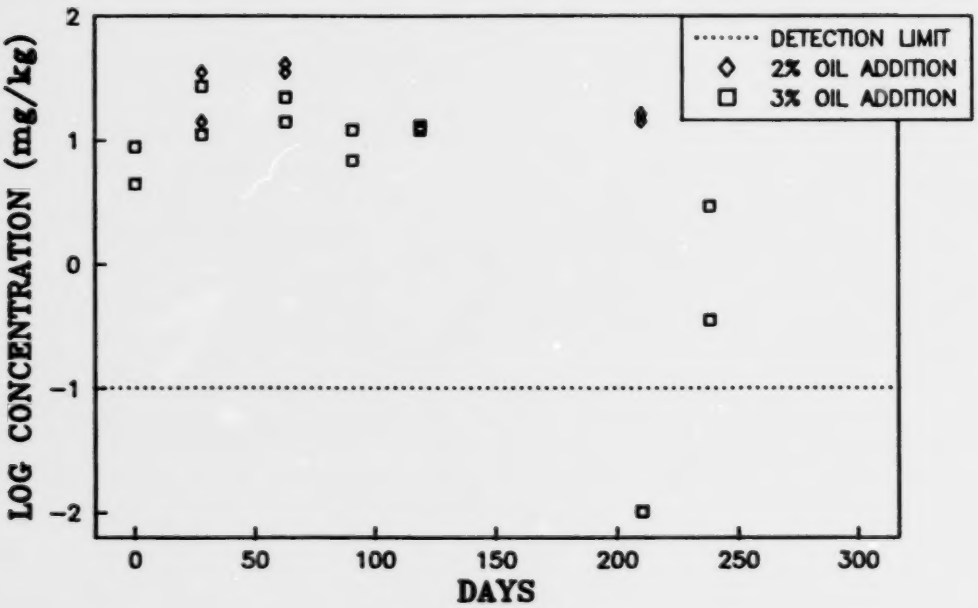


FIGURE 6.1.3 CONCENTRATION OF CHRYSENE IN WASTE TREATED SOIL

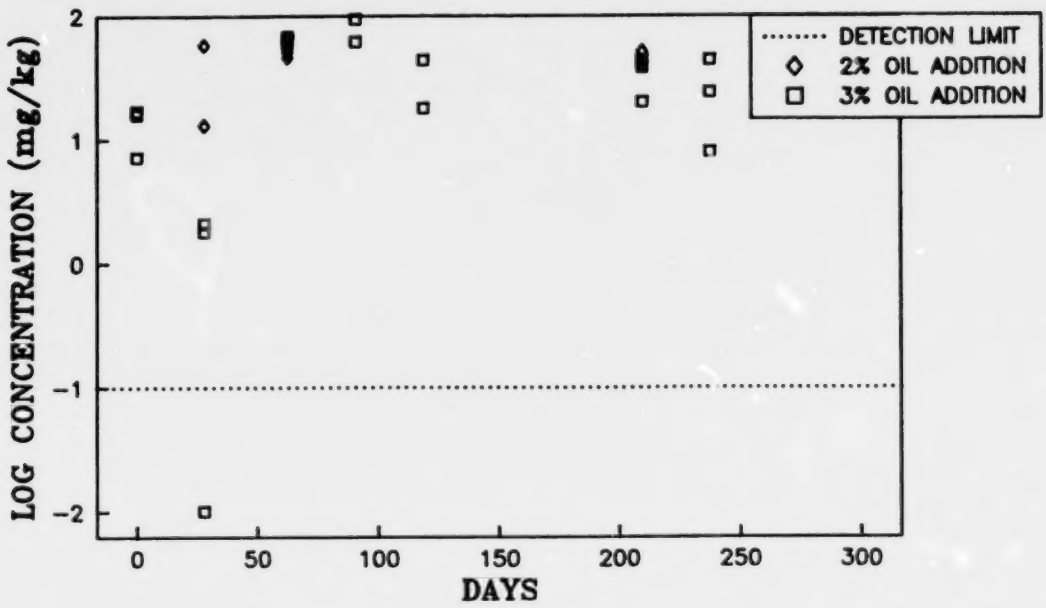


FIGURE 6.1.4 CONCENTRATION OF BENZO(A)ANTHRACENE IN WASTE TREATED SOIL

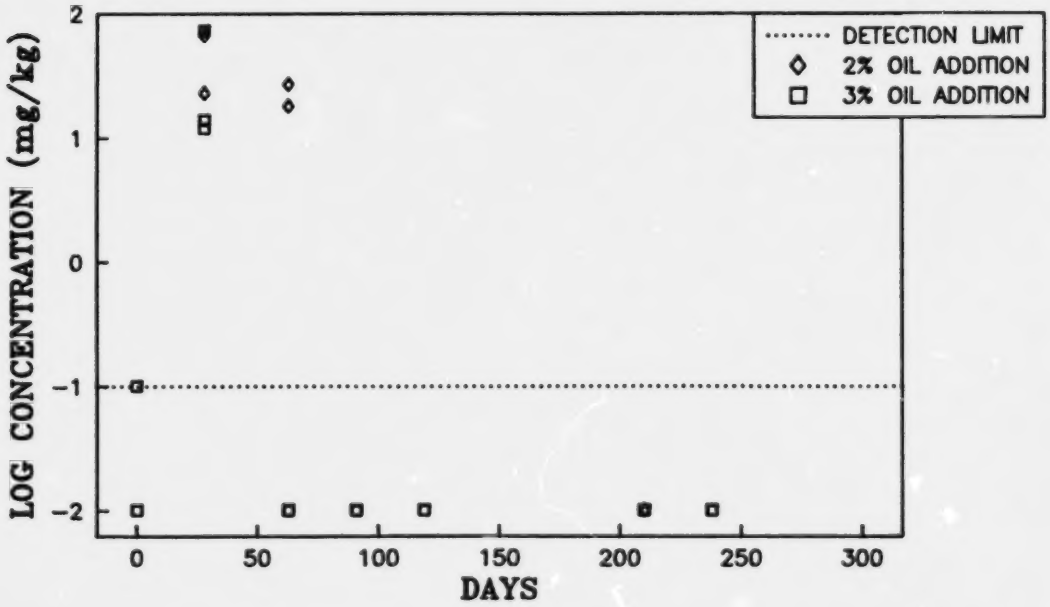


FIGURE 6.1.5 CONCENTRATION OF BENZO(B/K)FLUORANTHENE IN WASTE TREATED SOIL

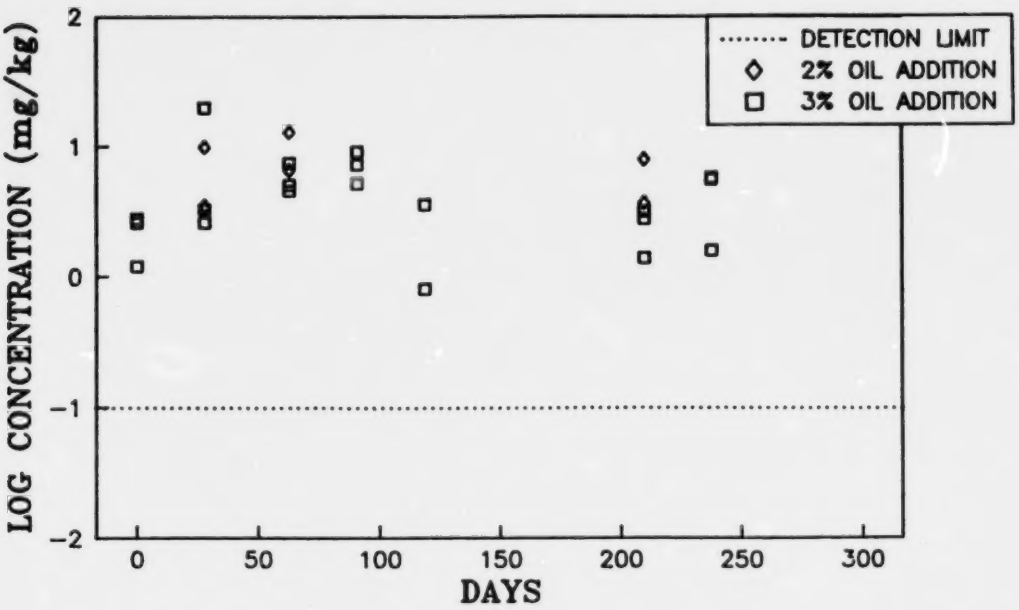


FIGURE 6.1.6 CONCENTRATION OF BENZO(A)PYRENE IN WASTE TREATED SOIL

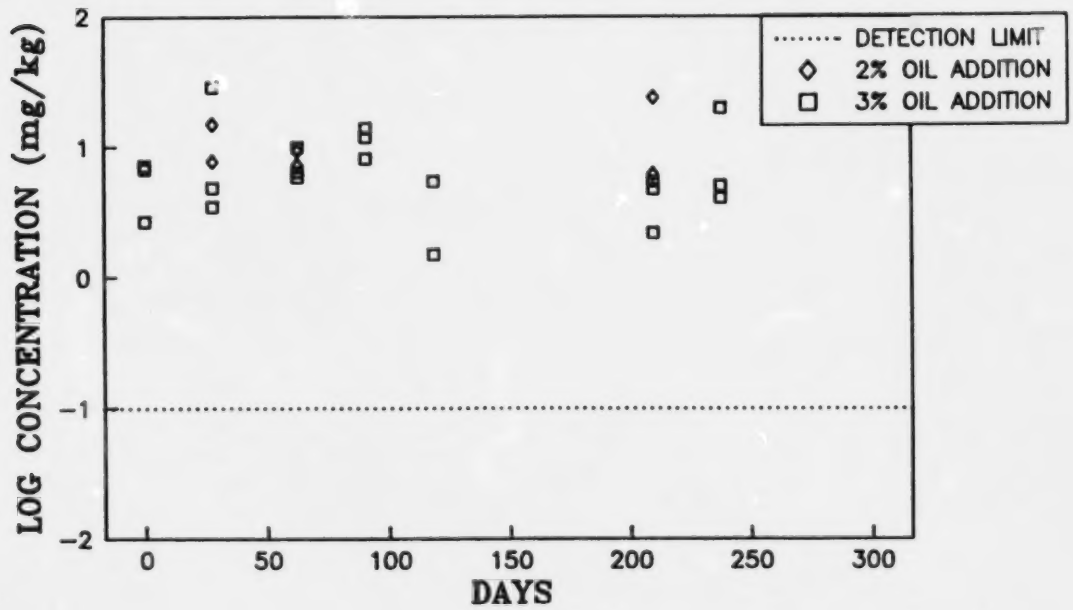


FIGURE 6.1.7 CONCENTRATION OF DIBENZO(A,H)ANTHRACENE IN WASTE TREATED SOIL

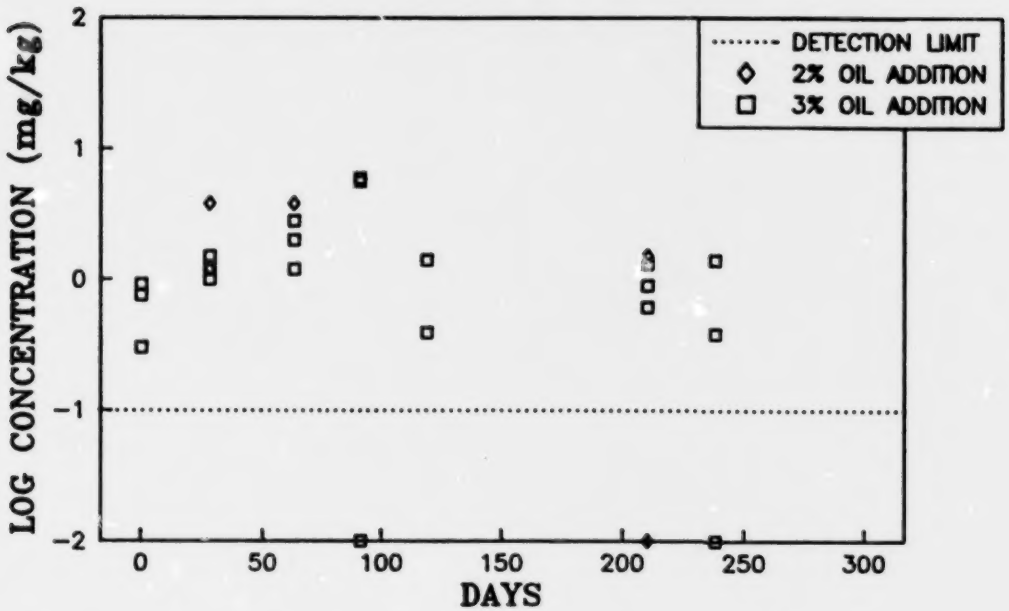


FIGURE 6.1.8 CONCENTRATION OF INDENO(1,2,3-C,D)PYRENE IN WASTE TREATED SOIL

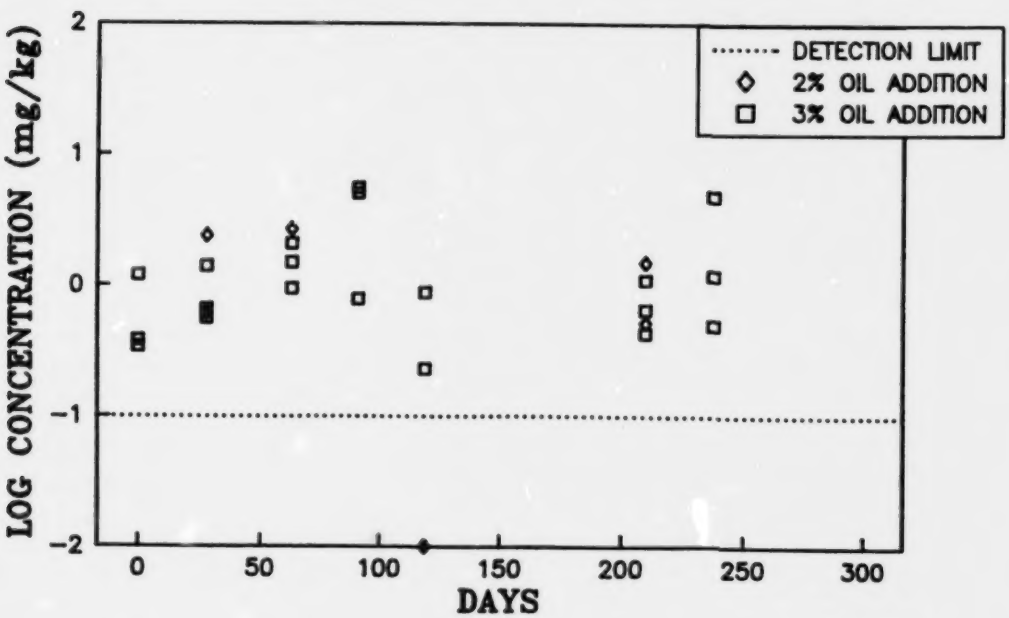


FIGURE 6.1.9 CONCENTRATION OF BENZO(G,H,I)PERYLENE IN WASTE TREATED SOIL

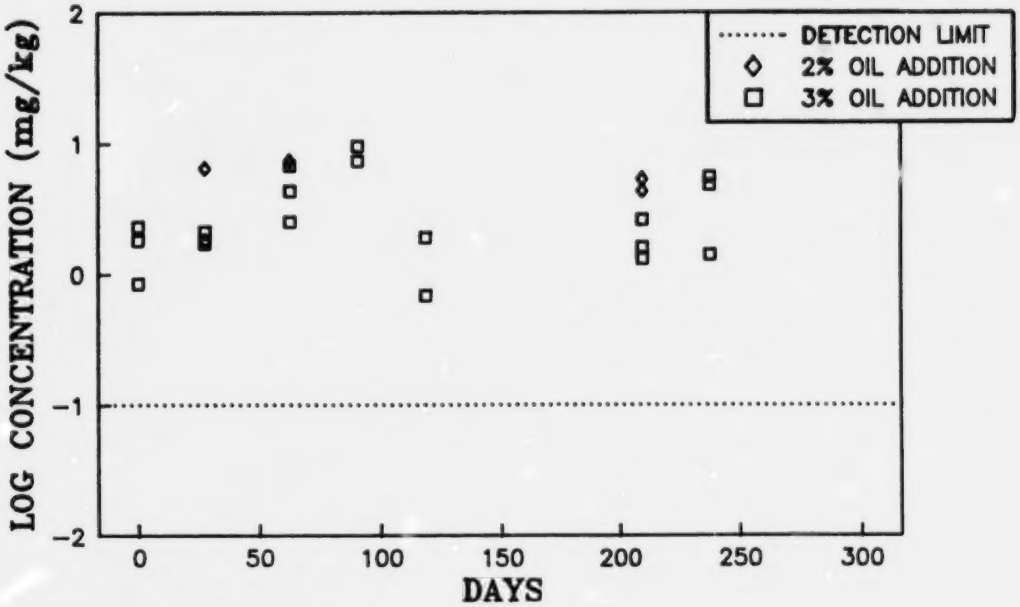
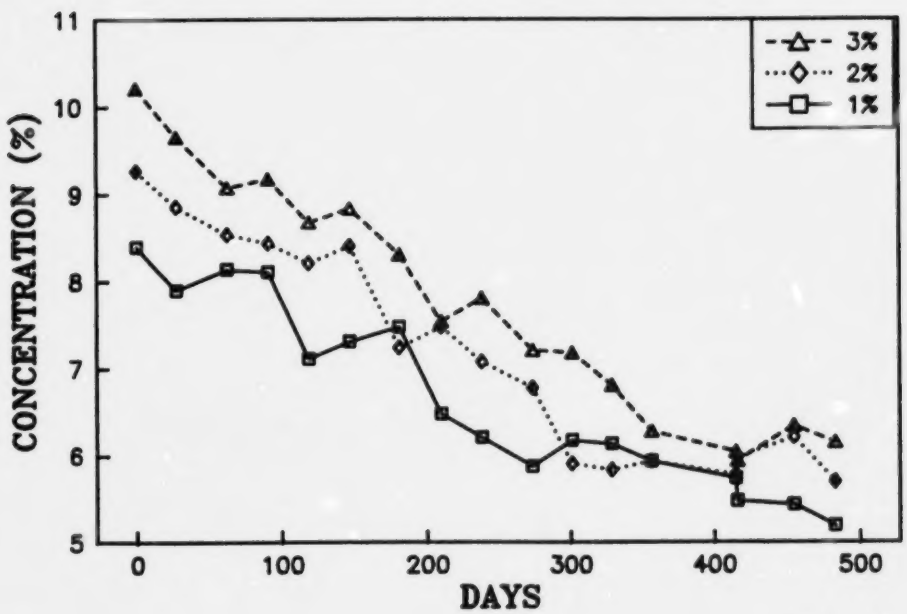


FIGURE 6.1.10 CONCENTRATION OF OIL IN WASTE TREATED SOIL (AVERAGE OF THREE REPLICATES)



6.2 Part 2 - Landfarm Sampling

The Part 2 study involved monitoring of soil at three operating landfarm sites to determine the persistence of target PAH's in soil under field conditions. In addition, groundwater was monitored at the three sites to determine if appreciable contamination of groundwater had occurred as a result of landfarm operations. The results are presented separately for each site and include a description of the waste application area, soil, waste and groundwater analysis.

6.2.1 Landfarm Site A

Refinery waste had been applied at site A for a period of three years prior to this study and continued during the period of monitoring. Applications of oily waste ranged up to 1% waste addition. Waste application was made by subsurface injection (at 6") followed by cultivation. The soil at site A is a clay loam, naturally imperfectly drained but with a tile drainage system installed at a depth of 30". The low levels and short history of application were reflected in low levels of both PAH and gross parameters in both soil and groundwater.

6.2.1.1 Soil

Initial levels of oil, metals, basic cations and total target PAH in background soil and soil which had been treated with oily waste are provided in Table 6.2.1.1.1. Parameters for soil which had received biosludge applications were not significantly different from those for background soil and are included in background data. The total target PAH is a summation of the concentrations of each of the 16 target PAH's. The detection limit for each PAH was 0.08 mg/kg. The low values for total target PAH in both background and oily waste treated subsoil consisted of a few PAH's at or near the limit of detection and were considered not significantly different from the background topsoil.

Table 6.2.1.1.1 Initial concentrations of gross parameters and total target PAH in background and oily waste treated soil at site A (averages of 4 samples).

		Background		Oily Waste Site	
		Topsoil	Subsoil	Topsoil	Subsoil
oil and grease	(%)	<0.01	<0.01	0.29	0.03
Calcium	(%)	0.64	0.54	0.73	0.67
Potassium	(%)	2.06	2.24	1.86	2.41
Magnesium	(%)	0.93	0.98	0.66	1.00
Sodium	(%)	0.75	0.70	0.71	0.72
Cadmium	(mg/kg)	0.07	<0.5	0.25	<0.5
Chromium	(mg/kg)	73.5	74.5	70.5	80.8
Lead	(mg/kg)	19.5	15.0	35.25	20.0
Zinc	(mg/kg)	120	111	143	122
pH		7.03	6.93	6.93	6.82
EC	(mS/cm^2)	0.30		0.44	
Total target PAH	(mg/kg)	ND*	0.23	0.46	0.22

* (below 0.08 mg/kg for each of 16 PAH)

Application of oily waste in 1985 took place on areas 1,2,3 and 4 (Figure 5.2.1.1a) at a level of approximately 0.12 L/m^2 over the periods 16 May to 22 July and 18 to 20 September. The concentration of PAH in sludge from site A is provided in Table 6.2.1.1.2. The PAH's in the table are organized in order of increasing molecular weight. Few of the higher molecular weight PAH's were detected in the sludge.

Table 6.2.1.1.2 Concentration of PAH's in sludge from site A

PAH	molecular weight	Concentration (mg/kg dry weight)
naphthalene	128	22.76
acenaphthalene	152	2.68
acenaphthene	154	13.01
phenanthrene	178	69.01
anthracene	178	4.88
fluoranthene	202	1.95
pyrene	202	5.20
chrysene	228	7.40
benzo(a)anthracene	228	ND
benzo(b)fluoranthene/ benzo(k)fluoranthene	252	0.81
benzo(a)pyrene	252	ND
indeno(1,2,3-c,d)pyrene	276	ND
dibenzo(a,h)anthracene	278	ND
benzo(g,h,i)perylene	276	ND

ND: not detected (below 0.08 mg/kg for each PAH)

Analysis of soil over the entire incubation period indicated a level of total target PAH roughly similar to that of 1/100 of the sludge concentration. The proportions that individual PAH's contributed to the total target PAH content were different for the soil than the sludge, however, and changed over the course of the monitoring period. Figure 6.2.1.1.1 illustrates the proportions of the total target PAH made up by PAH's of similar molecular weights for soil and sludge samples.

Figure 6.2.1.1.1 illustrates the total target PAH concentration (height of the stacked bar) as well as the concentrations of individual PAH weight fractions (length of individual shaded segments). The sludge sample, illustrated here at 1/100 concentration, is dominated by low molecular weight PAH's in the 128 to 178 molecular weight range (naphthalene, acenaphthylene, acenaphthene, phenanthrene and anthracene), whereas the soil samples are dominated by higher molecular weight PAH's, primarily in the 202 to 228 molecular weight range (fluoranthene, pyrene, chrysene, benzo(a)anthracene) and, later in the year, including the 252 to 278 molecular weight PAH's (benzo(b/k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene). The low molecular weight PAH's (molecular weight 128 to 178) are both more volatile and more easily degraded than the higher molecular weight compounds and would not be persistent when applied to the soil. The appearance of high molecular weight PAH's, which were not at detectable levels in the sludge or early sample periods, may have been due to chemicals which were present in early

samples but were not detected due to interferences by lower molecular weight compounds which did not persist in later samples.

Individual fingerprint diagrams (Figures 6.2.1.1.2-6) illustrate the concentrations of individual PAH's in oil treated soil and the sample variability associated with each. Background concentrations of PAH's, in previous studies, ranged from 0 to 0.3 mg/kg (Bulman et al., 1985). Background concentrations at Site A were similar, generally ranging from 0 to 0.2 mg/kg with one sample from the biosludge area containing 0.65 mg/kg phenanthrene. Concentrations of PAH's in the oily waste-treated soil ranged from 0 to 1.5 mg/kg, however, no PAH was consistently detected (i.e. in at least 3 of 4 replicates) at a level greater than 0.2, with the single exception of benzo(a)anthracene in the August 1985 sample period. Although the total target PAH content of several samples exceeded that of background soil at the end of the monitoring period. There is no statistically significant evidence that landfarm operations have increased the PAH content in soil on this site within the four year operating period.

The variability of these samples is high. A high level of sample variability would be expected, as a relatively small amount of a heterogeneous material (oily refinery waste) was added to a large volume of soil. Analytical variability is also high for this type of sample and especially at concentrations approaching the detection limit in soil. In these samples, the distinction between observed concentrations and background (0.2 mg/kg) or not detected (less than 0.08 mg/kg) concentrations of PAH was less than the inherent variability of the samples. The results of assessment of analytical variability are presented in Appendix B.

The concentration of oil in the waste treated soil was generally low. Figure 6.2.1.1.7 illustrates the concentration and variability of oil in the soil over the monitoring period. Mean oil concentrations reflect an increase with waste application and a subsequent decrease with time. Sample variability was high, however, and differences in concentration with time were not significant.

Metal concentrations were generally low and no consistent trend with time was observed. No relationship between oil, metal or PAH concentrations was observed, probably because the concentrations did not significantly differ from background levels. Table 6.2.1.1.3 summarizes the final concentrations of gross parameters and total target PAH in the oil treated soil at the end of the monitoring period.

Table 6.2.1.1.3 Final concentrations of gross parameters and total target PAH in oily waste treated soil at site A (average of 4 samples).

oil and grease	(%)	0.23
Calcium	(%)	1.61
Potassium	(%)	2.56
Magnesium	(%)	1.17
Sodium	(%)	0.77
Cadmium	(mg/kg)	<0.5
Chromium	(mg/kg)	69.8
Lead	(mg/kg)	27.3
Zinc	(mg/kg)	116
pH		7.40
EC	(mS/cm^2)	0.49
Total PAH	(mg/kg)	1.56

The total target PAH content appeared to have increased over the monitoring period. It must be kept in mind, however, that this value consists of a summation of several values, each of which were close to the detection limit.

6.2.1.2 Groundwater

Groundwater was sampled from a total of five wells at a 4 - 5 ft. depth over the May to October, 1985 field season. One well in the centre of the waste application area, well 8, was also sampled at a depth of 12 ft. Figures 6.2.1.2.1 and 6.2.1.2.2 illustrate the concentrations of dissolved organic carbon (DOC) and total target PAH, respectively, in samples collected from the wells at the beginning of the field season, superimposed on the landfarm site plan. In the figures, data are located adjacent to the corresponding well locations. According to company reports, groundwater flow was generally from north to south, but the groundwater gradient was minimal and local flow varied seasonally. Well 1 (to extreme left of site plan) was therefore considered the control, or background, well and the others were considered downstream wells. In certain instances, insufficient sample was obtained from the wells for both PAH and DOC analysis. Occasionally, certain wells were completely dry.

The data in Figure 6.2.1.2.1 suggest that the DOC loading to groundwater was somewhat elevated downstream of the waste application area. The differences in DOC concentrations are small, however, and may not be significant. Data for total PAH's in Figure 6.2.1.2.2 also indicate somewhat higher concentrations in downstream wells, although the variations in concentration do not correspond exactly to those of the DOC values.

Concentrations of DOC and total target PAH at the end of the field season are illustrated in Figures 6.2.1.2.3 and 6.2.1.2.4. Little change in DOC was observed, however, total target PAH concentrations were somewhat lower.

Concentrations of DOC and total target PAH observed over the entire monitoring period are presented in Figures 6.2.1.2.5 and 6.2.1.2.6, respectively. Data points are missing for wells with insufficient sample

volume. Data from well 8 is presented for both the 4 - 5 ft. depth (8C) and the 12 ft. depth (8B). Concentrations of DOC ranged from 6.3 to 9.5 mg/L in the background well and from 6.9 to 17.5 mg/L in downstream wells. Values were consistently lowest in the control well. Peak DOC loadings were in the spring and fall sample periods and may have been the result of greater hydraulic loadings during those periods.

Total target PAH concentrations ranged from not detected to 0.27 µg/L in the background well and from not detected to 0.76 µg/L in downstream wells. Concentrations of total target PAH exceeded the background range in well 8B (12 ft. depth) in April, in well 8C (4 - 5 ft. depth) in May and in well 2C in June. Concentrations generally decreased over the monitoring period and did not appear to correspond to DOC loadings.

The proportions of PAH molecular weight groups in groundwater samples varied between wells and over the course of the monitoring period. As the concentrations of individual PAH's were generally close to the detection limits, however, the values are imprecise. In the background well samples, concentrations of all molecular weight groups were generally less than 0.1 µg/L.

As observed for total PAH concentrations, the concentration of individual PAH's peaked in the April to June period and did not exceed background concentrations from July to October. Anthracene (molecular weight 178) was the predominant constituent in wells 4, 6, and 8B in the April sample period, with concentrations of 0.15 to 0.2 µg/L (detection limits 0.02 0.06 µg/L). Anthracene was not, however, a dominant constituent of the waste applied to the site or of the soil. The concentration of anthracene in groundwater over the monitoring period is illustrated in Figure 6.2.1.2.7.

Chrysene (molecular weight 228) was the predominant constituent in well 8C in May, at 0.4 µg/L (detection limits 0.08). Chrysene was also detected at significant concentrations in the soil in the April to June period. The concentration of chrysene in groundwater is illustrated in Figure 6.2.1.2.8.

Benzo(a)anthracene concentrations in wells 2, 6 and 8B in the June sample period exceeded those observed in the background well on this site, but were within the range (up to 0.1 µg/L) observed in background wells from site C. The concentration of benzo(a)anthracene in groundwater is illustrated in Figure 6.2.1.2.9.

Although certain PAH's appeared to occur in groundwater at slightly elevated concentrations in downstream wells, the concentration and frequency of occurrence was not sufficient to conclude that they originate from the waste application activities on the site.

FIGURE 6.2.1.1.1 PROPORTIONS OF PAH'S IN SITE A LANDFARM TOPSOIL GROUPED BY MOLECULAR WEIGHT

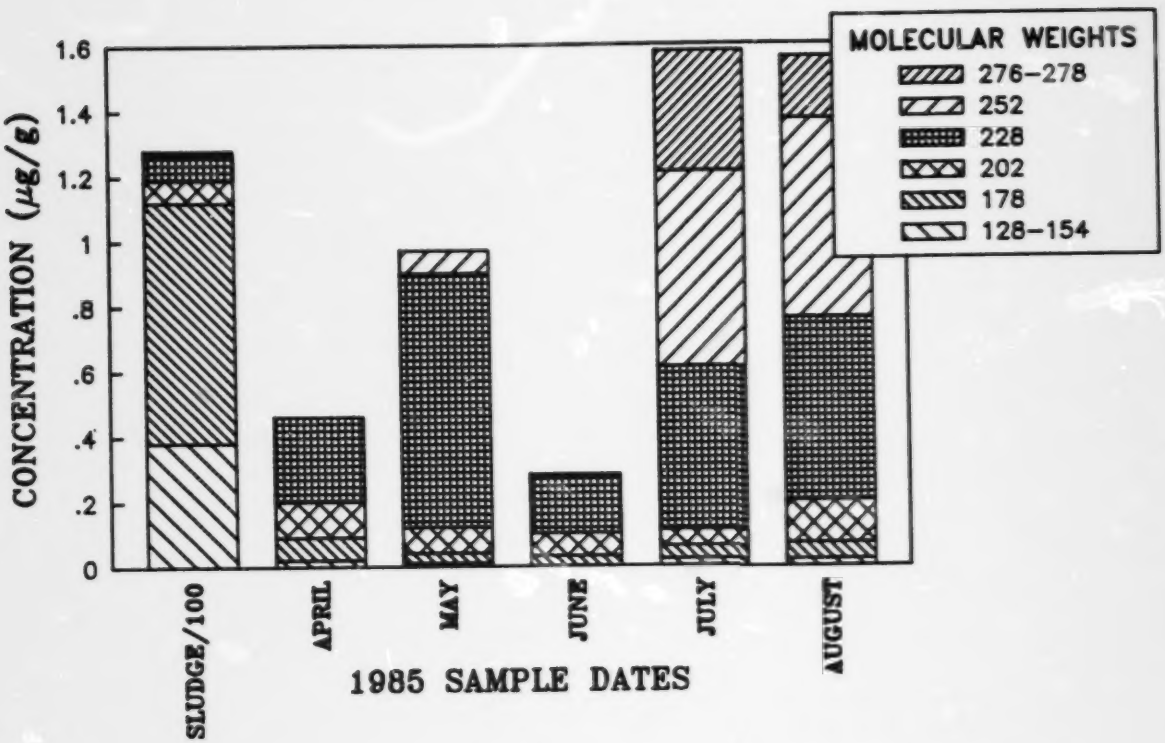


FIGURE 6.2.1.1.2 FINGERPRINT OF PAH'S IN SITE A TOPSOIL
APRIL 1985

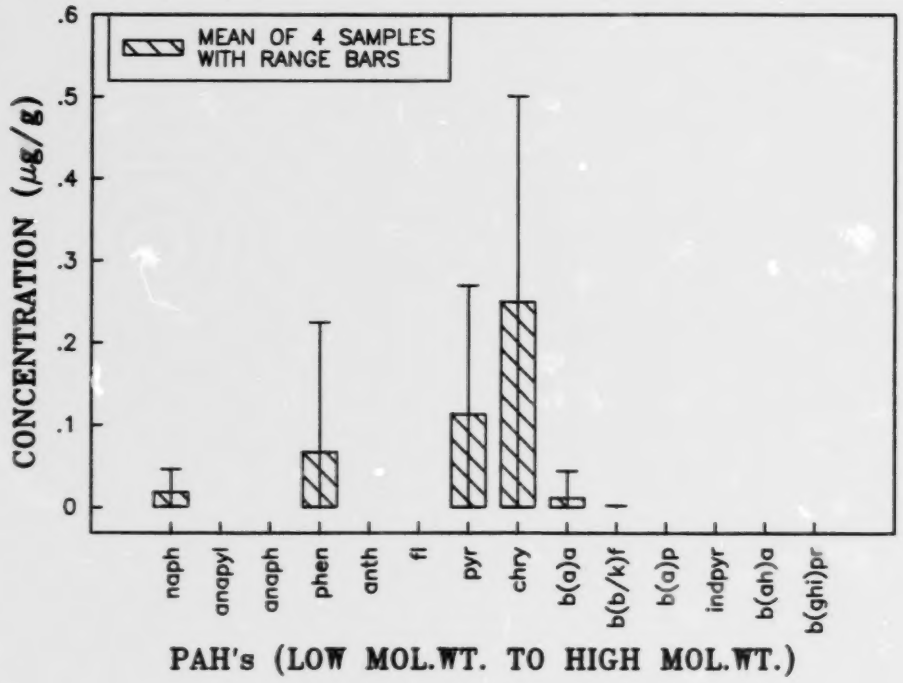


FIGURE 6.2.1.1.3 FINGERPRINT OF PAH'S IN SITE A TOPSOIL
MAY 1985

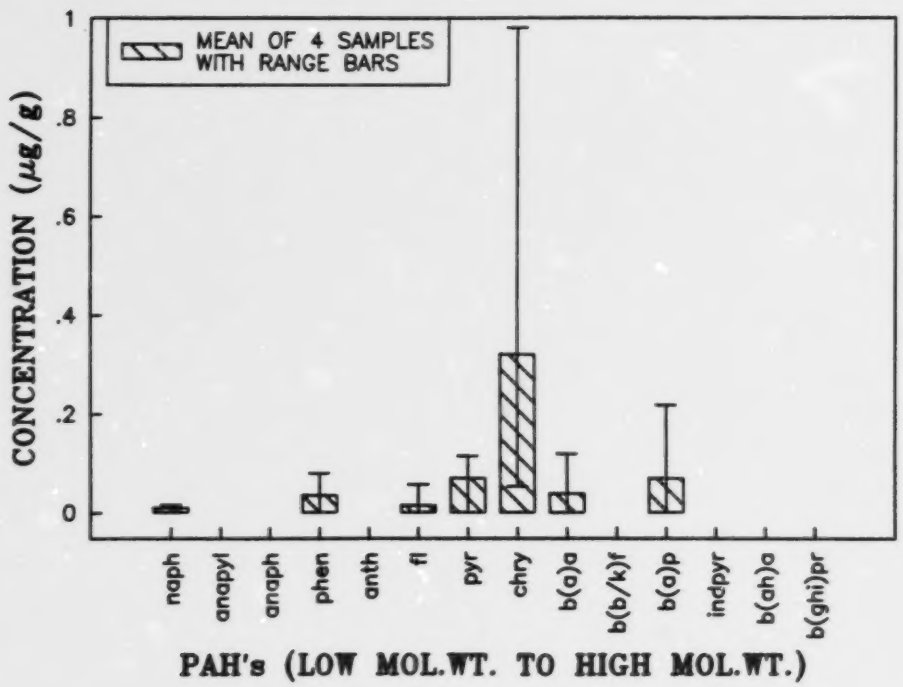


FIGURE 6.2.1.1.4 FINGERPRINT OF PAH'S IN SITE A TOPSOIL
JUNE 1985

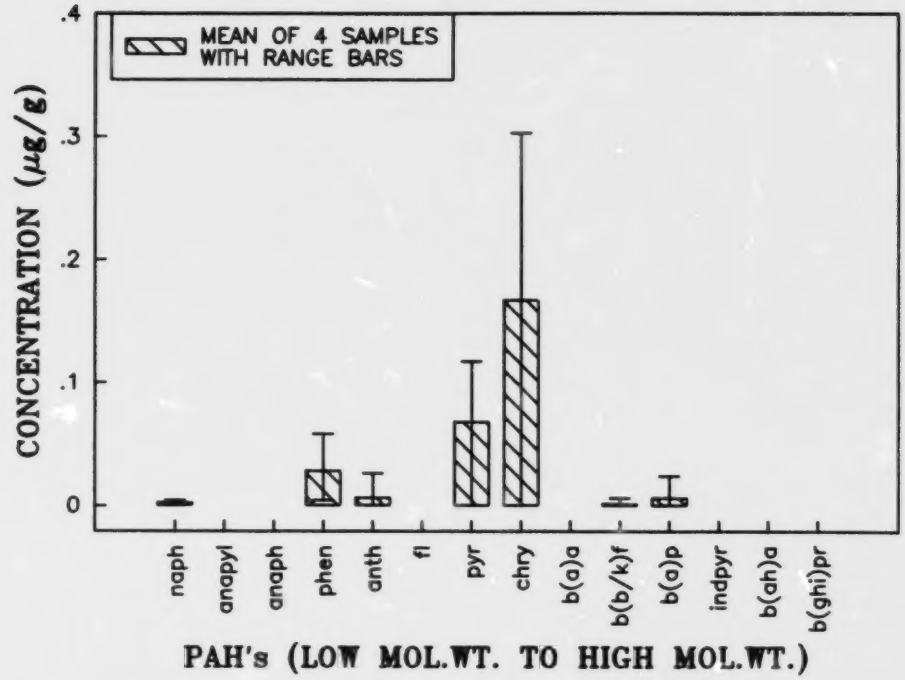


FIGURE 6.2.1.1.5 FINGERPRINT OF PAH'S IN SITE A TOPSOIL
JULY 1985

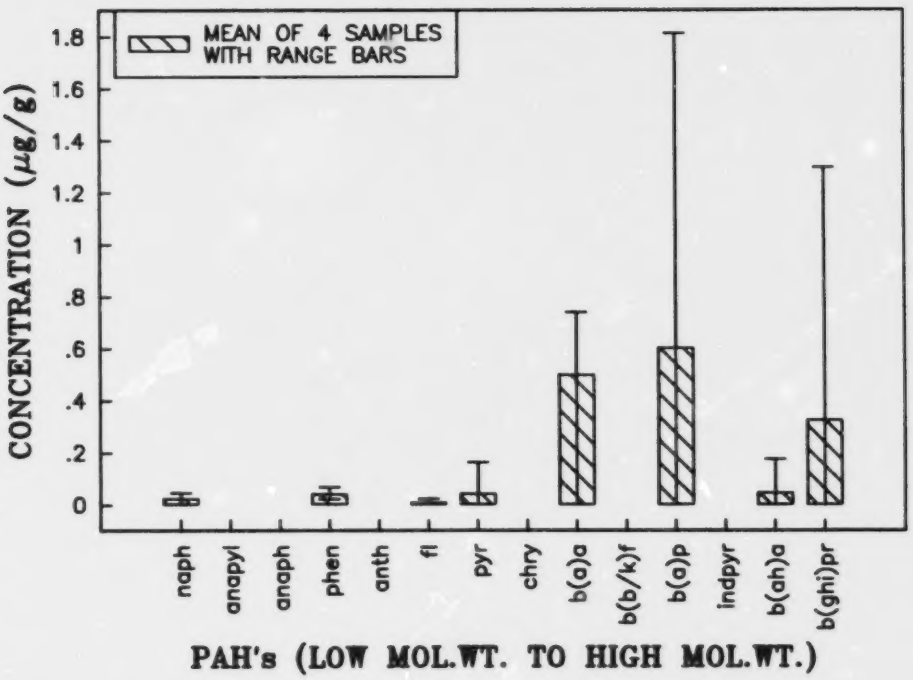


FIGURE 6.2.1.1.6 FINGERPRINT OF PAH'S IN SITE A TOPSOIL
AUGUST 1985

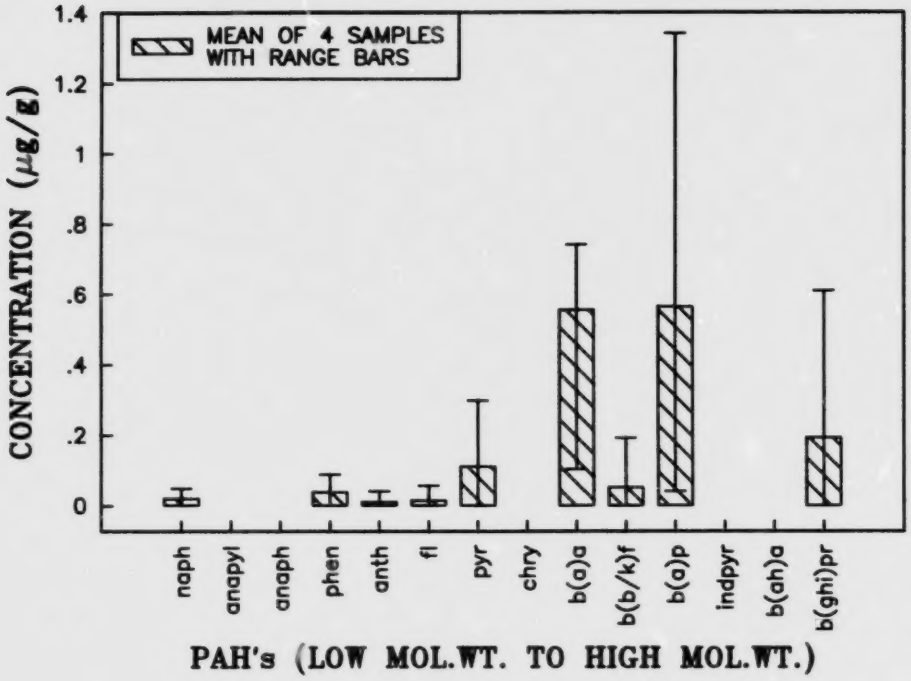


FIGURE 6.2.1.1.7 OIL IN SITE A TOPSOIL

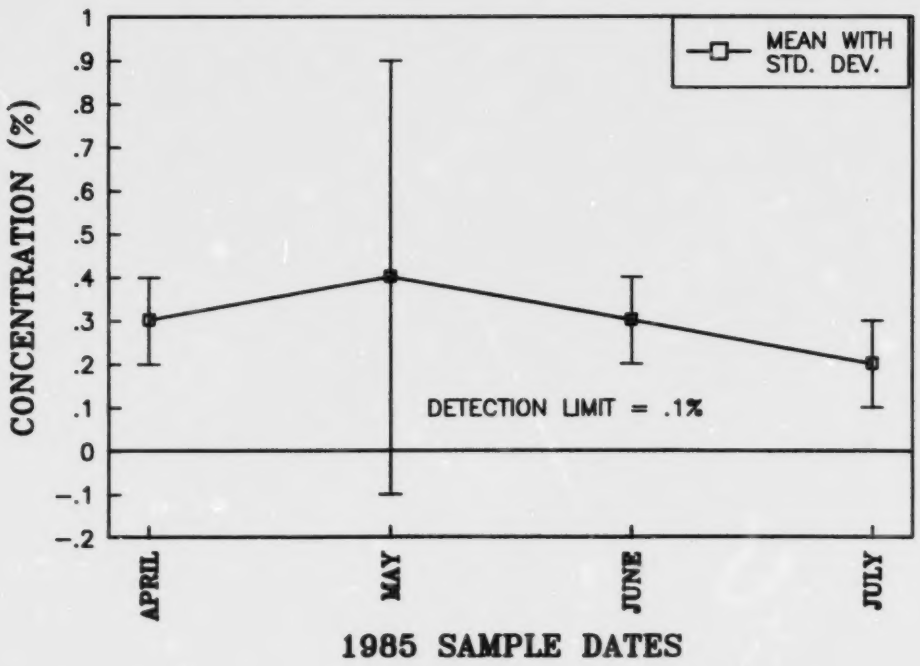


FIGURE 6.2.1.2.1 DOC IN WELLWATER (mg/L) SITE A
APRIL 1985

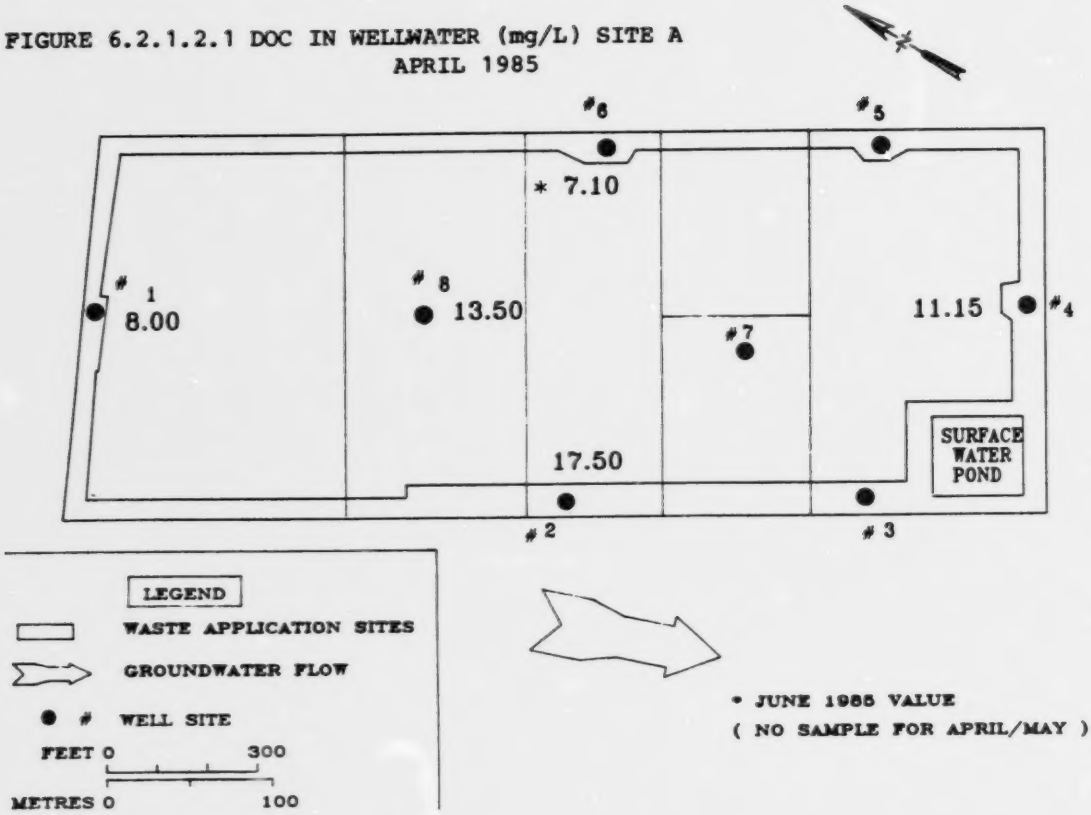


FIGURE 6.2.1.2.2 TOTAL PAH IN WELLWATER (µg/L) SITE A
APRIL 1985

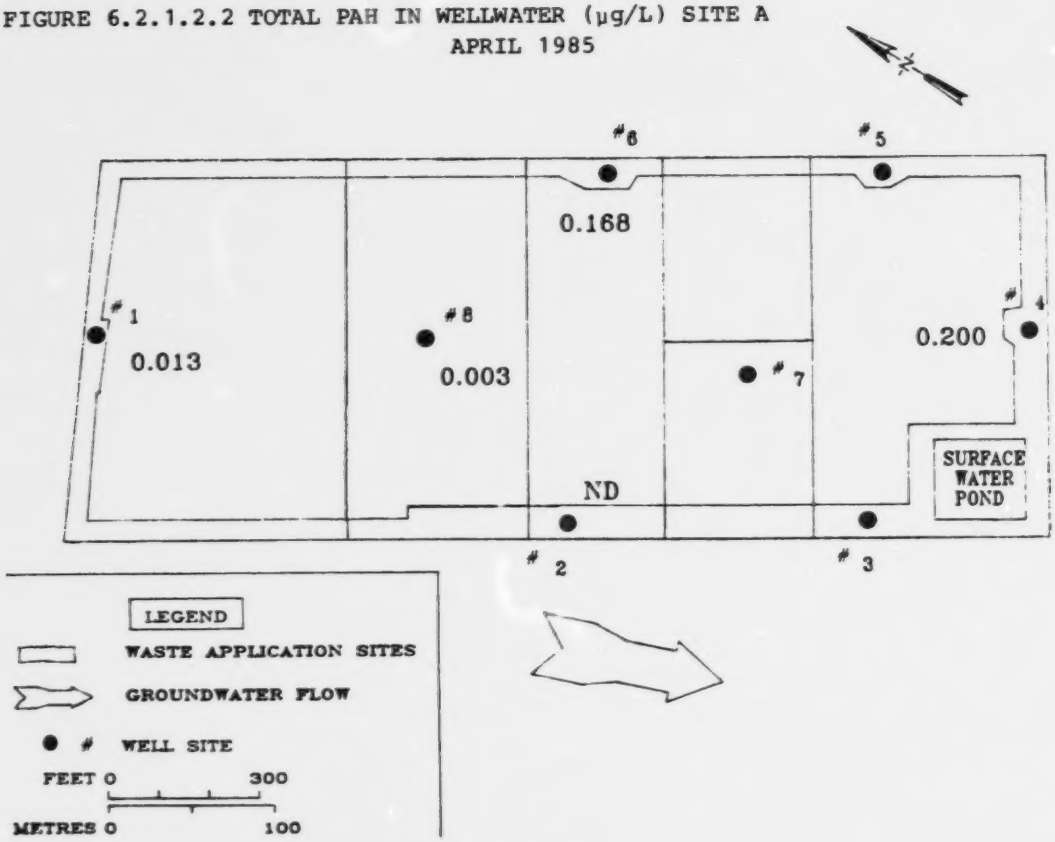


FIGURE 6.2.1.2.3 DOC IN WELLWATER (mg/L) SITE A
OCTOBER 1985

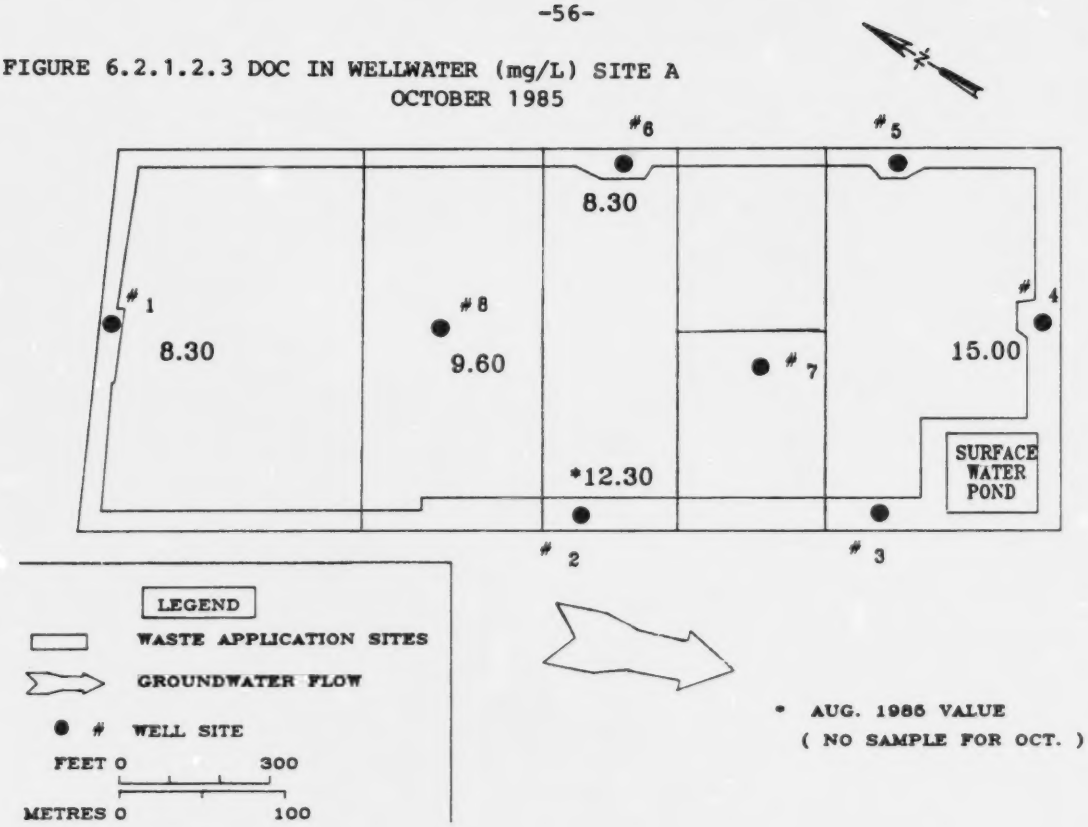


FIGURE 6.2.1.2.4 TOTAL PAH IN WELLWATER (µg/L) SITE A
OCTOBER 1985

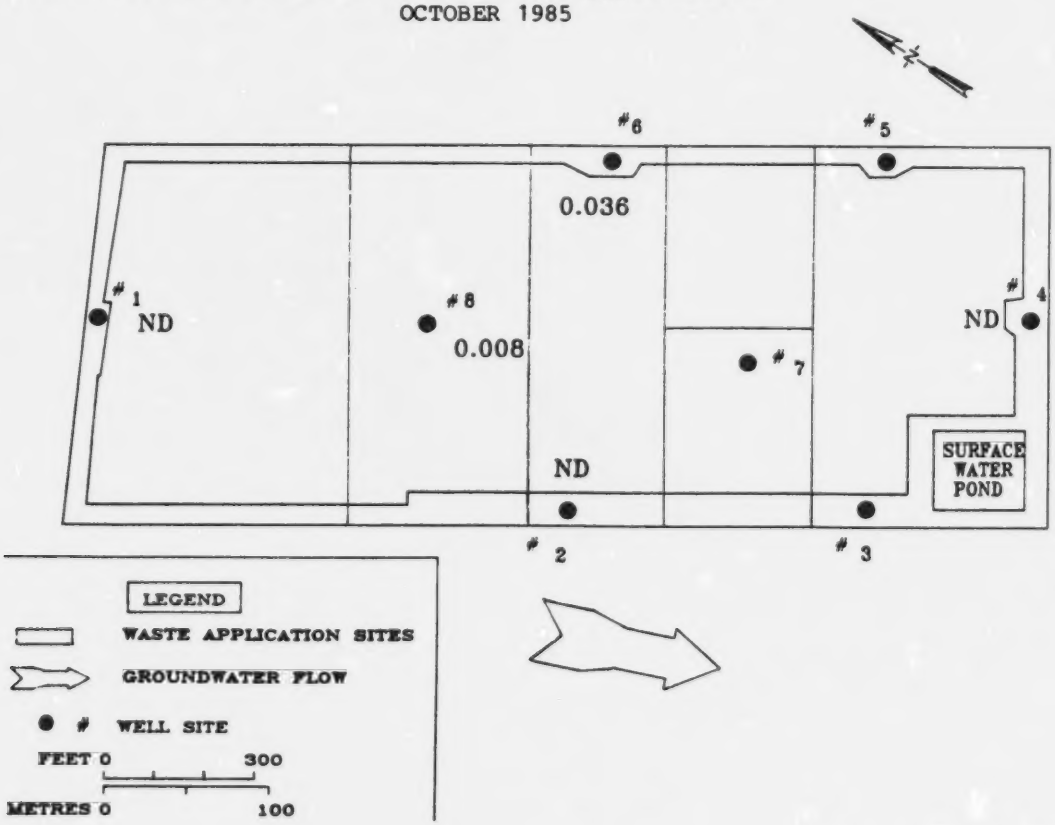


FIGURE 6.2.1.2.5 DOC IN SITE A WELLWATER THROUGHOUT 1985

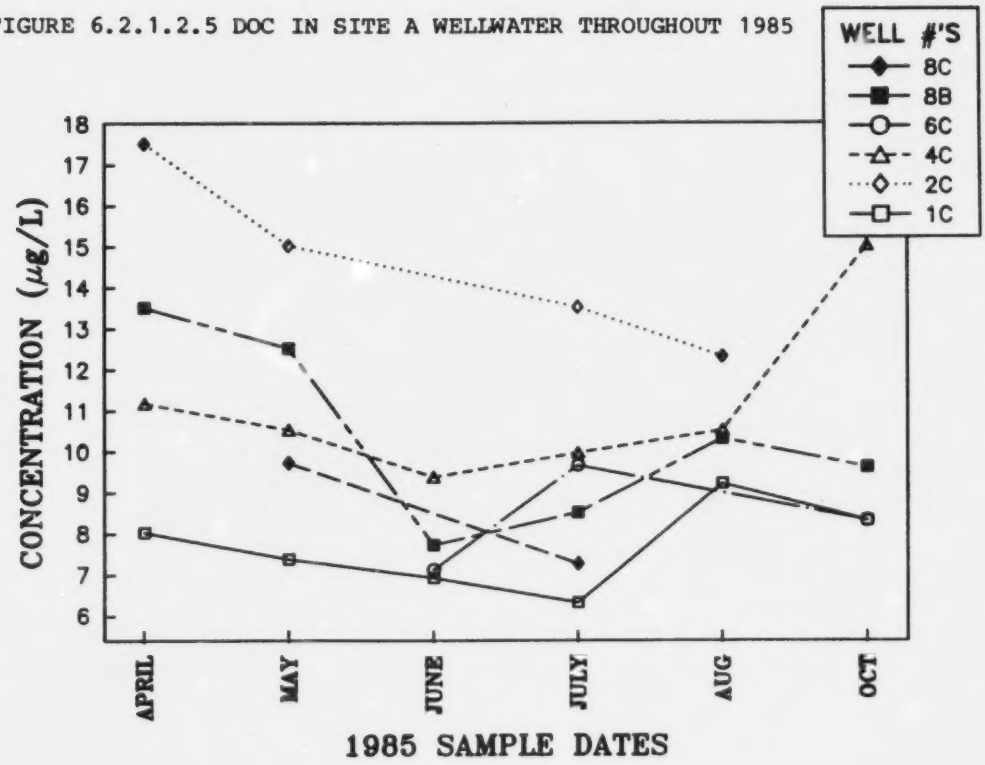


FIGURE 6.2.1.2.6 TOTAL PAH IN SITE A WELLWATER THROUGHOUT 1985

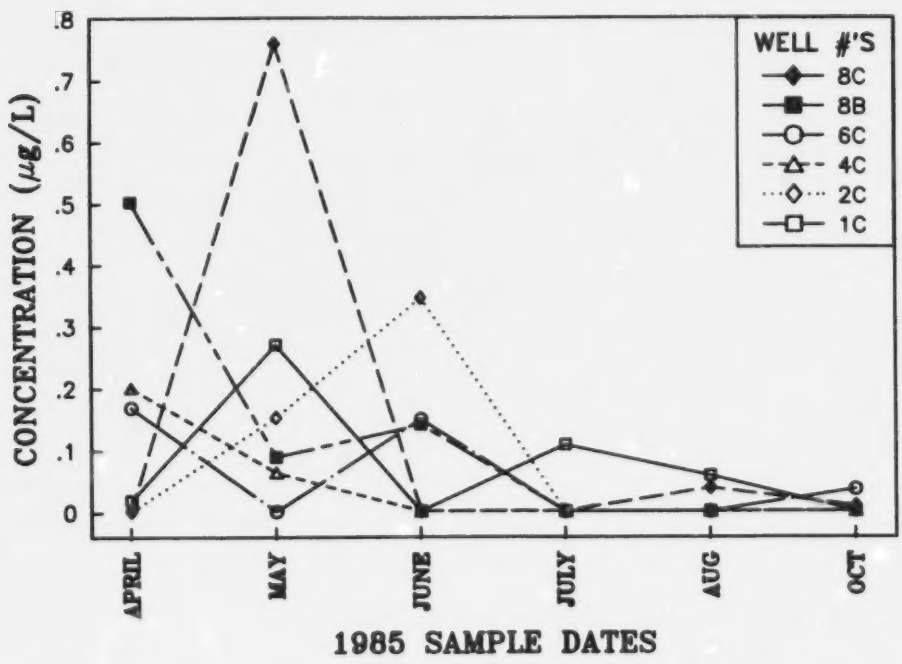


FIGURE 6.2.1.2.7 CONCENTRATION OF ANTHRACENE IN SITE A WELLWATER

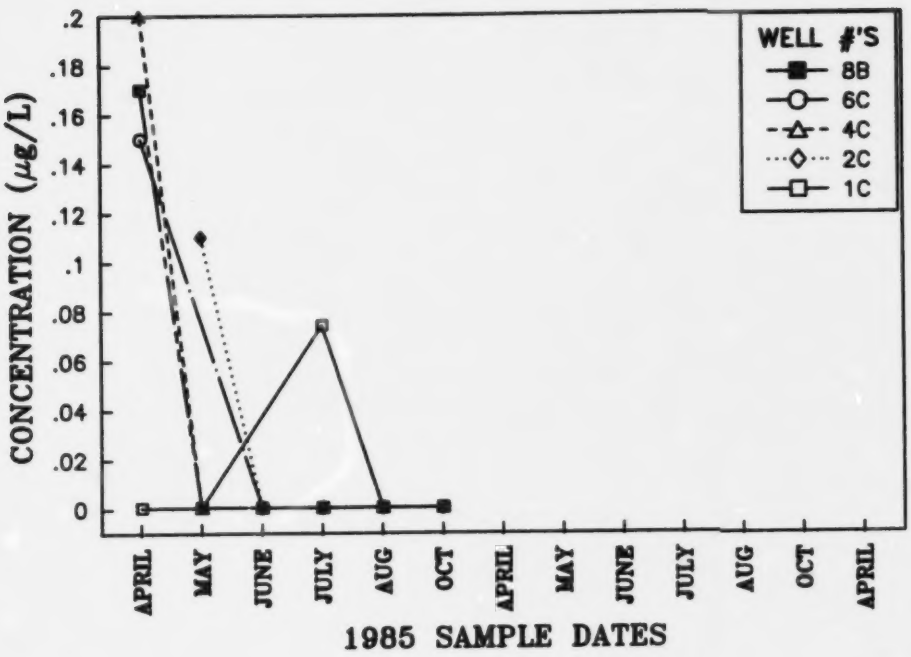


FIGURE 6.2.1.2.8 CONCENTRATION OF CHRYSENE IN SITE A WELLWATER

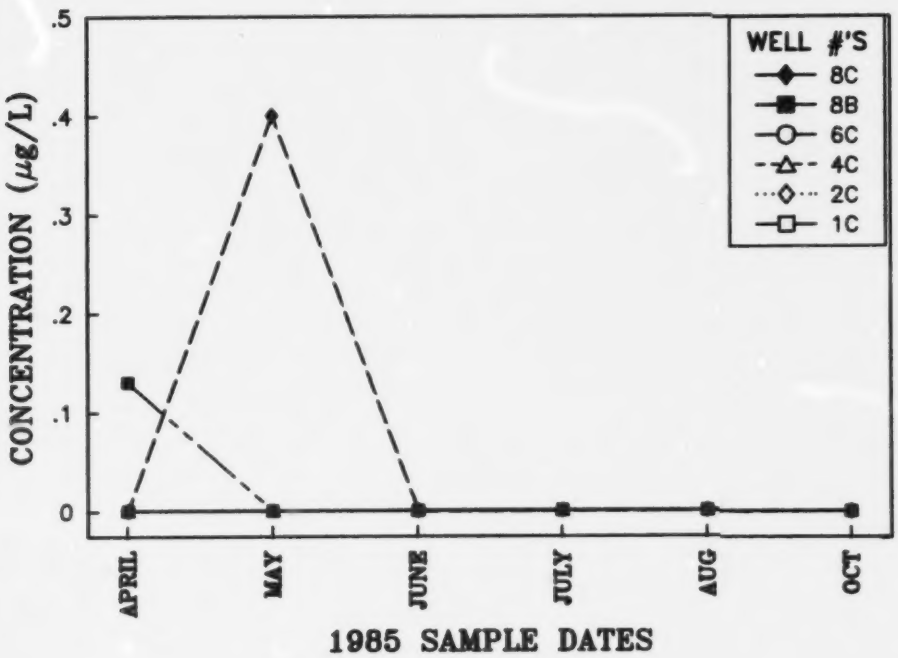
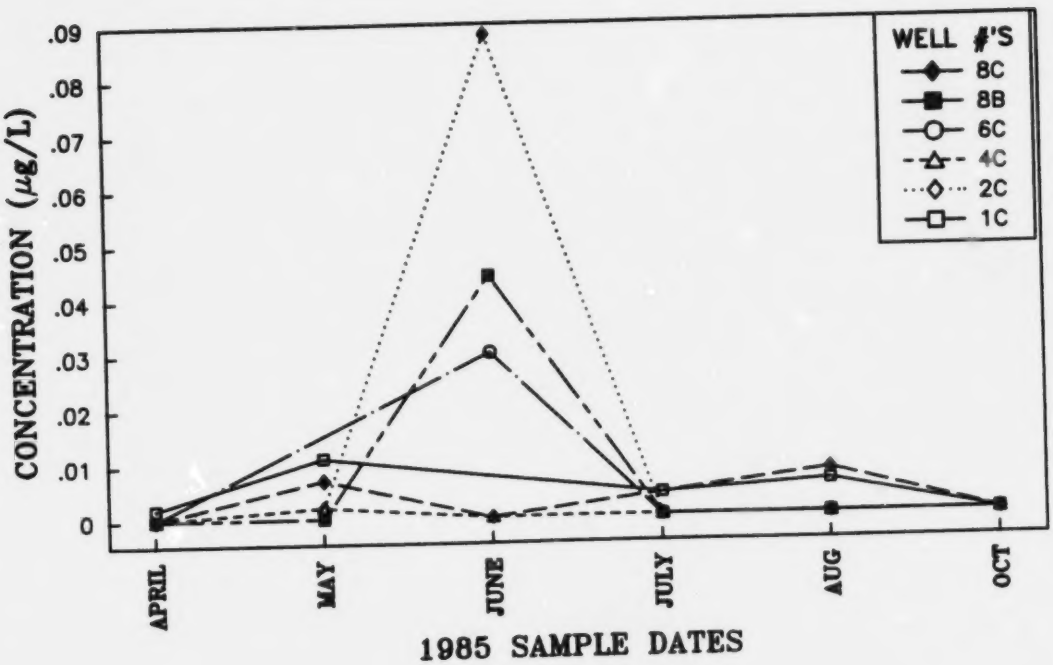


FIGURE 6.2.1.2.9 CONCENTRATION OF BENZO(A)ANTHRACENE IN SITE A WELLWATER



6.2.2 Landfarm Site B

Site B was located on a silt loam soil, which was imperfectly drained and of neutral pH. The site was located within the area of refinery operations, and down-gradient from both the tank farm areas and the refinery process area.

The site had been operated as a landfarm for a period of approximately 10 years prior to this study. Recent landfarm operation involved waste application followed by cultivation twice yearly. Fertilizer was not applied. During the course of this study, waste was applied to the main portion of the site. One portion of the site was left uncultivated and supported vegetation during the year prior to, and including, the year of this study. Samples taken from the uncultivated portion of the site were composited and analysed separately as a blocked replicate, designated as replicate 3 in the reported results. Average data are reported for replicates 1 and 2.

6.2.2.1 Soil

Initial soil parameters, such as oil, metals, basic cations and total target PAH are provided in Table 6.2.2.1.1 for control soil and soil taken from the landfarm site. Detailed soil texture data is unavailable. Total PAH data is also unavailable for the background soil, as the sample was lost (destroyed).

Table 6.2.2.1.1 Initial concentrations of gross parameters and total target PAH in background and oily waste treated soil at site B.

	Background	Oily Waste Site	
	Avg	Avg	Rep 3
oil and grease (%)	0.70	1.45	2.60
Calcium (%)	0.80	1.70	1.30
Potassium (%)	2.20	2.13	1.49
Magnesium (%)	0.85	1.03	0.70
Sodium (%)	0.59	0.66	0.71
Cadmium (mg/kg)	<0.5	<0.5	<0.5
Chromium (mg/kg)	220	470	743
Lead (mg/kg)	34	70.0	101
Zinc (mg/kg)	198	357	515
pH		6.65	6.90
EC (mS/cm^2)		-	
Total target PAH (mg/kg)*		2.35	0.54

* sample taken after waste application in 1984

It is apparent that a history of waste application has increased the oil, metal and Ca concentration in the soil. It is possible that infrequent cultivation on replicate 3 resulted in greater oil accumulation, but this effect was not apparent for PAH concentration.

Application of oily waste was made at a level of 51 and 40 m^3/ha (0.9% oil

on a wet weight basis) in July and August of 1984, respectively, 95 m^3/ha in August, 1985 (0.14% oil) and 47 m^3/h in September, 1985 (0.62% oil).

The concentrations of PAH's in sludge from the site B refinery, reported in Table 6.2.2.1.2, was similar to that from site A.

Table 6.2.2.1.2 Concentration of PAH's in sludge from site B.

PAH	molecular weight	Concentration (mg/kg dry weight)
naphthalene	128	8.46
acenaphthylene	152	17.31
acenaphthene	154	11.31
phenanthrene	178	57.7
anthracene	178	9.23
fluoranthene	202	2.69
pyrene	202	9.04
chrysene	228	5.00
benzo(a)anthracene	228	ND
benzo(b)fluoranthene/ benzo(k)fluoranthene	252	0.46
benzo(a)pyrene	252	ND
indeno(1,2,3-c,d)pyrene	276	ND
dibenzo(a,h)anthracene	278	ND
benzo(g,h,i)perylene	276	ND

ND: not detected (below 0.08 mg/kg for each PAH)

Analysis of soil indicated that the total concentration of PAH in waste treated soil increased substantially in the latter part of the field season on both cultivated and uncultivated portions of the site. Figures 6.2.2.1.1 and 6.2.2.1.2 illustrate the proportions of the total target PAH (total height of stacked bar) made up by PAH groups (length of individual shaded segments) of similar molecular weight in soil and sludge samples. Over the May and June period, the concentration of total target PAH was similar to that of 1/100 of the sludge concentration on both cultivated and uncultivated portions of the site. Samples taken in July, 1985 for both replicates of the cultivated portion of the site were lost (destroyed). The total concentration of PAH in August, 1985 samples, however, were significantly higher than previously observed. This corresponds to waste application to the site in August. The concentration of total target PAH in replicate 3 samples, from the uncultivated area, were significantly higher in July, 1985 than previously observed and decreased somewhat in August, 1985. This pattern does not correspond to the timing of waste application.

As previously observed for site A, the proportion of higher molecular weight PAH's was greater in the soil than in the sludge. In addition, the proportion of PAH in the 276-278 molecular weight range was greater in samples taken toward the end of the field season. As suggested for site A, analysis of the high molecular weight PAH in early sample periods may have been impeded by compounds which were lost from soil in later sample

periods. In contrast to site A, the increase in concentration in later sample periods was observed for all molecular weight groups, probably as a result of waste application to the site.

Individual fingerprint diagrams are presented in Figures 6.2.2.1.3-5 and Figures 6.2.2.1.6-9 to illustrate the concentrations of individual PAH's in cultivated and uncultivated soil, respectively, over the sampling period. Concentrations of both replicates and the means are presented for the cultivated area. Concentrations for the uncultivated area are for one sample. The fingerprints of PAH's were very similar for the cultivated and uncultivated plots.

Concentrations of fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene exceeded levels observed as background on sites A and C (0.2 mg/kg). These PAH's may have been added to soil in the current or previous applications of sludge. Benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were not detected in the sludge applied in the current year, although this may have been due to interferences in analysis by compounds which did not persist in soil. The concentrations of these PAH also appeared to increase over the field season. To some extent, this was likely due to waste application. Also, changes in the effect of the oily soil matrix on analysis may be responsible.

Plots of concentration over the monitoring period for those PAH's which exceeded the background concentrations are presented in Figures 6.2.2.1.10-16. Data for replicate 3 consists of one sample only. Both replicates and the mean are presented for replicates 1 and 2. Keeping in mind that there is no July data for the cultivated plot to compare with the uncultivated plot, the trends observed on the two plots were similar. Data for the August period was, however, extremely variable. Trends were observed for chrysene (decrease with time) and dibenzo(a,h)anthracene and benzo(g,h,i)perylene (increase with time), as indicated by ranges for initial and final concentrations which do not overlap. An insufficient number of samples were available to test the statistical significance of these trends. The concentrations of fluoranthene, pyrene, benzo(a)anthracene and benzo(a)pyrene may also have increased with time, but the data was too variable to draw any conclusions. Due to the limited number of samples taken and the variability among samples, the data was not suitable for kinetic modelling.

Replicate 2 often contained concentrations of PAH much higher than replicate 1 which resulted in the highly variable results for many samples. The composite for replicate 2 included a sample taken from a portion of the cultivated area which was in a slight depression, received run-off water from the rest of the site and was often ponded and too wet to be cultivated. It is likely that more oily waste material collected in that area than on the rest of the site, contributing to higher PAH values in that sample.

Variability in the results may also be due to analytical variability in recovery through extraction or cleanup, as well as subsample variability, i.e. within the composite sample. Analytical variability was observed to be high and is discussed in Appendix B.

The concentration of oil increased following waste application in the fall

of 1984. The mean concentration decreased by approximately 0.8% oil with time, returning to the original concentration by July of 1985. No increase in oil content was apparent following waste application in August, possibly due to the low content of oil in the waste. Figure 6.2.2.1.17 illustrates the concentration (+/-standard deviation) of oil in soil averaged for all replicates (cultivated and uncultivated). As observed previously, a high degree of sample variability was observed and there were no significant differences in oil content with time.

The concentrations of zinc, lead and chromium were related to the concentration of oil in the soil, as illustrated in Figure 6.1.2.1.18. No relationship between total target PAH and oil was apparent, although increasing levels of chromium and zinc may have been associated with the higher PAH concentrations, as illustrated in Figure 6.1.2.1.19. Table 6.2.2.1.3 summarizes the final concentrations of gross parameters and total target PAH in the waste treated soil at the end of the monitoring period.

Table 6.2.2.1.3 Final concentrations of gross parameters and total PAH in oily waste treated soil at site B.

	Avg	Rep 3
oil and grease (%)	1.45	2.60
Calcium (%)	1.85	1.81
Potassium (%)	2.25	1.69
Magnesium (%)	1.22	0.98
Sodium (%)	0.67	0.83
Cadmium (mg/kg)	<0.5	<0.5
Chromium (mg/kg)	423	484
Lead (mg/kg)	76.0	114
Zinc (mg/kg)	357	440
pH	7.25	7.19
Total target PAH (mg/kg)	12.78	6.73

No net increase in oil or metal content was apparent at the end of the monitoring period. The concentration of metals in some cases appeared reduced at the end of the period, but this is likely due to sample variability. Total target PAH concentration did appear to increase substantially on both cultivated and uncultivated plots.

6.2.2.2 Groundwater

Sampling of wells at site B began with 3 wells in November and December of 1984 and continued with 7 wells from May to October, 1985. Information on well installation was not available and not many wells were available for sampling. The interpretation of groundwater data was therefore severely limited.

Wells 8 and 9 were selected to provide background water quality data on the basis that they were remote from the landfarm area under study. Wells 11 and 16 may also have been suitable choices as background wells, however they were close to the site and the local groundwater flow patterns were not precisely known. There were no other suitable upgradient wells. One offsite well originally had been installed as a control well, but the

casing was broken off at ground level and the well was thus uncapped and subject to contamination from site maintenance equipment. Although wells 8 and 9 are located within the operating refinery area and could potentially be affected by refinery operations, total target PAH concentrations were low and comparable to background levels observed at sites A and C.

Figures 6.2.2.2.1 and 6.2.2.2.2 illustrate the concentrations of dissolved organic carbon (DOC) and total target PAH, respectively, in samples collected from wells throughout the site in May 1985. The direction of groundwater flow on the site is roughly northwest to southeast, according to a consultant's report (unpublished).

Background DOC values were observed in the range 11.0 to 21.0 mg/kg. Wells near the landfarm site contained DOC levels ranging from 5.6 to 46.5 mg/kg. Inspection of Figure 6.2.2.2.1 suggests that organic loading of groundwater was greater to the southeast and south of the waste application site than to the north and west of the site. Dissolved organic carbon was substantially greater than background levels in well 13, south of the waste application area.

Background levels of total target PAH's were no more than .55 µg/L. Wells near the landfarm area to the north and west contained levels up to 0.81 µg/L, while well 13, to the south, contained 1.45 µg/L. These data suggest that PAH concentrations were somewhat elevated in proximity to the waste application area. The highest PAH concentration corresponded to the well with the highest DOC value, although PAH concentrations were not generally related to DOC.

Figures 6.2.2.2.3 and 6.2.2.2.4 provide similar information for DOC and total PAH concentrations in samples taken in the August monitoring period. The DOC values ranged from 2.7 to 17.9 mg/kg. The pattern of elevated DOC values was consistent with that observed in May. Total target PAH concentrations had decreased and dropped to below detection limits in one well. As observed in May, well 13 contained total PAH concentrations above background levels.

The variations in DOC and total target PAH concentration over the monitoring period are illustrated in Figures 6.2.2.2.5 to 6.2.2.2.10. Data for the background wells are illustrated in Figures 6.2.2.2.5 and 6.2.2.2.6, respectively. Peak DOC loadings were in May, 1985. The total target PAH concentrations were also at a maximum in May and increased slightly in August and October.

Data for the wells on the north and west side of the landfarm (wells 11, 15 and 16) are presented in Figures 6.2.2.2.7 and 6.2.2.2.8. The DOC concentrations were similar to those in background wells with the exception of a very high concentration in December, 1984 (both replicates). The trends with time were similar to those observed for control wells. The total target PAH concentration for well 11 was in some cases greater than observed in background wells, however the trends observed with time were similar.

Well 14, to the east, and 13, to the south, generally contained higher DOC and total target PAH concentrations, (Figures 6.2.2.2.9 and 6.2.2.2.10). Peak DOC loadings were observed in December, May and October. The trend

was similar to that observed for other wells, but the fluctuation in concentration was greater. Peak PAH loadings were observed in December 1984 for well 14, but in May and July for well 13.

Individual PAH's did not exceed 0.1 µg/L in background wells. PAH's which exceeded background concentrations in the north and west side wells were phenanthrene, anthracene and pyrene, illustrated in Figures 6.2.2.2.11 to 6.2.2.2.13. Detection limits for individual PAH's are presented in Appendix B. The detection limits and background concentrations were exceeded generally in the May to August period, with the exception of pyrene which was also observed in well 11 in November 1984. Phenanthrene, anthracene and pyrene were also observed as constituents of the sludge applied to the site.

Wells 13 and 14 contained substantially higher concentrations of PAH's, particularly in the 128-154 and 202 molecular weight groups. The detection limits for the 128-154 molecular weight group is high and values observed near the limit, including those which account for the high total target PAH value for well 14 in November and December, 1984, are not precise. The detection limits and background concentrations were substantially exceeded, however, in well 13 by acenaphthylene (1.8 µg/L, detection limit 1 µg/L) in July, 1985 and in both wells by phenanthrene, fluoranthene and pyrene in the May - June period, 1985 (Figures 6.2.2.2.14 to 6.2.2.2.16). All four PAH's were observed in the waste.

Some contamination of groundwater, particularly to the south and east of the landfarm does appear to have taken place. This pattern is not consistent with the reported groundwater flow pattern. It was noted, however, that prior to the monitoring period some soil excavation had been performed to the south of the waste application site. This disturbance may have altered local groundwater flow patterns and, as it occurred on soil previously used for waste application, may have resulted in accelerated movement of soil contaminants into the groundwater.

Although the constituents found in groundwater were also constituents of the oily waste, the landfarm could not be positively identified as the source of increased organic loadings, due to the siting of the landfarm within the overall refinery operation.

FIGURE 6.2.2.1.1 PROPORTIONS OF PAH'S IN SITE B LANDFARM TOPSOIL GROUPED BY MOLECULAR WEIGHT - BLOCKS 1 AND 2

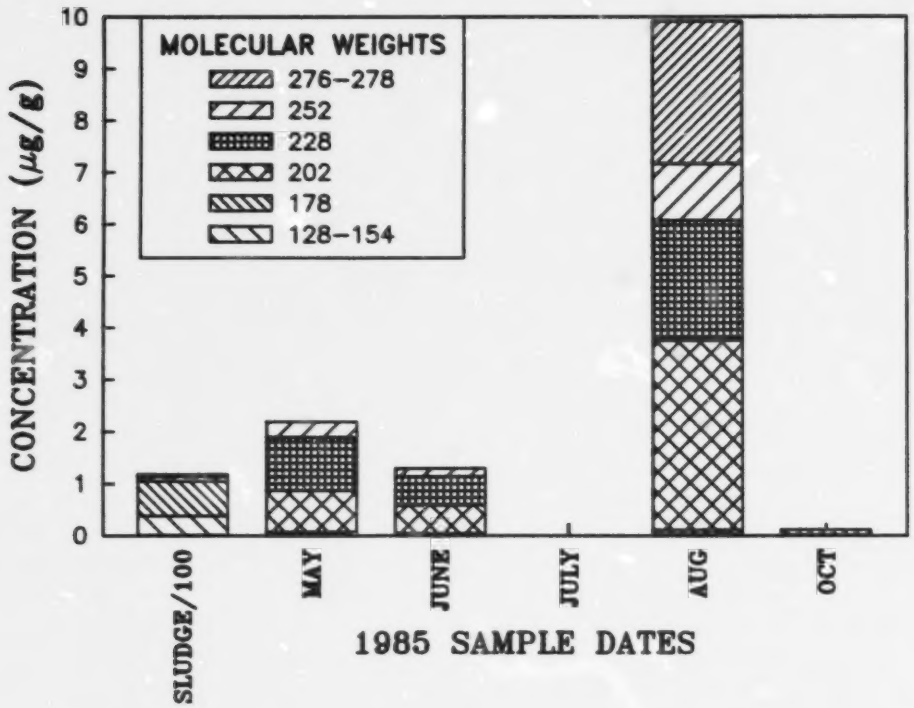


FIGURE 6.2.2.1.2 PROPORTIONS OF PAH'S IN SITE B LANDFARM TOPSOIL GROUPED BY MOLECULAR WEIGHT - BLOCK 3

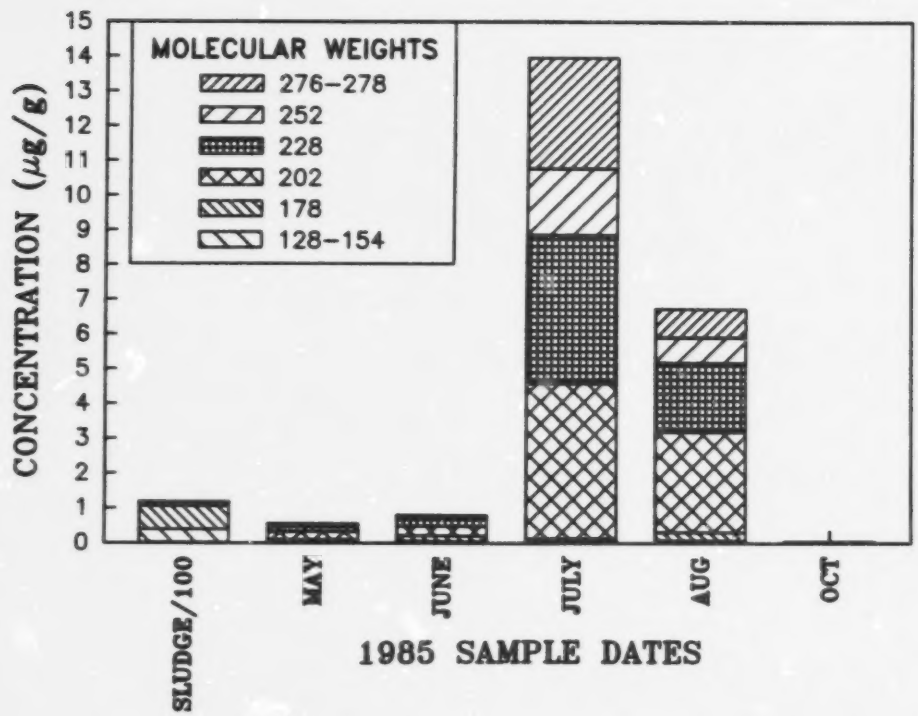


FIGURE 6.2.2.1.3 FINGERPRINT OF PAH'S IN SITE B TOPSOIL
BLOCKS 1 AND 2 - MAY 1985

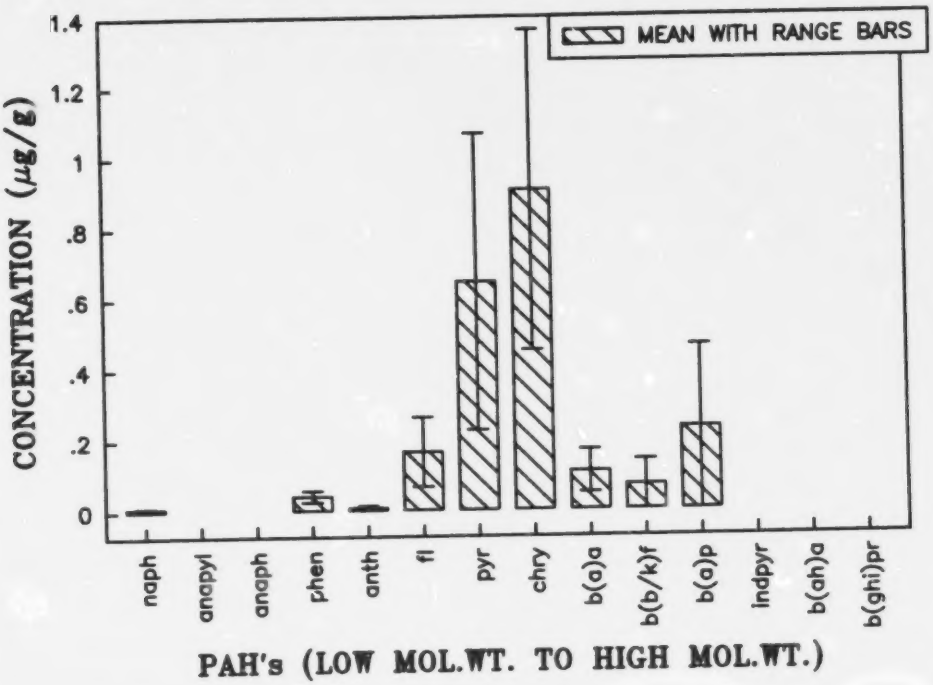


FIGURE 6.2.2.1.4 FINGERPRINT OF PAH'S IN SITE B TOPSOIL
BLOCKS 1 AND 2 - JUNE 1985

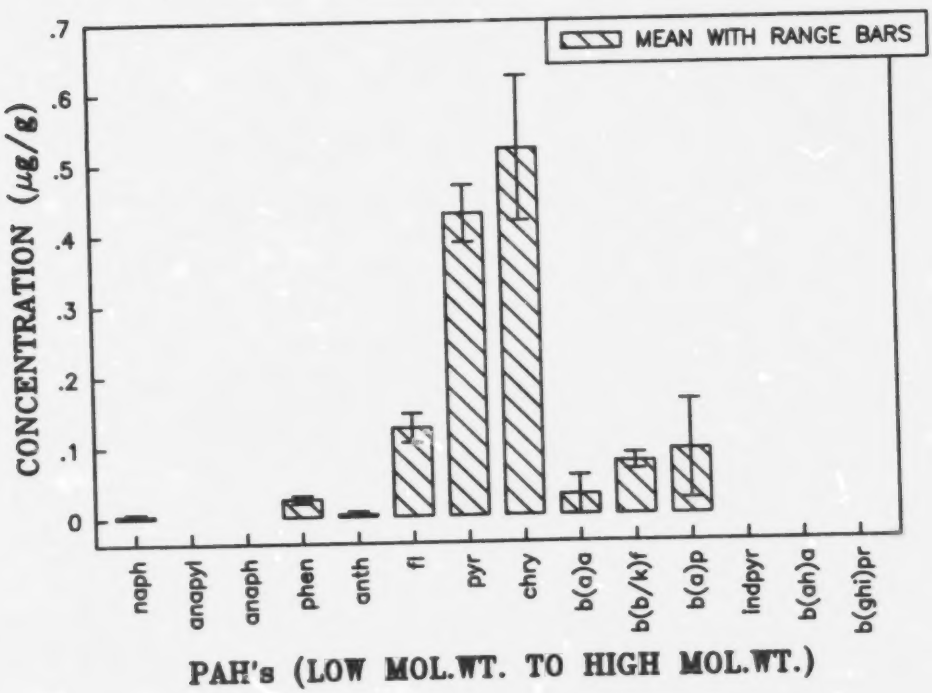


FIGURE 6.2.2.1.5 FINGERPRINT OF PAH'S IN SITE B TOPSOIL
BLOCKS 1 AND 2 - AUGUST 1985

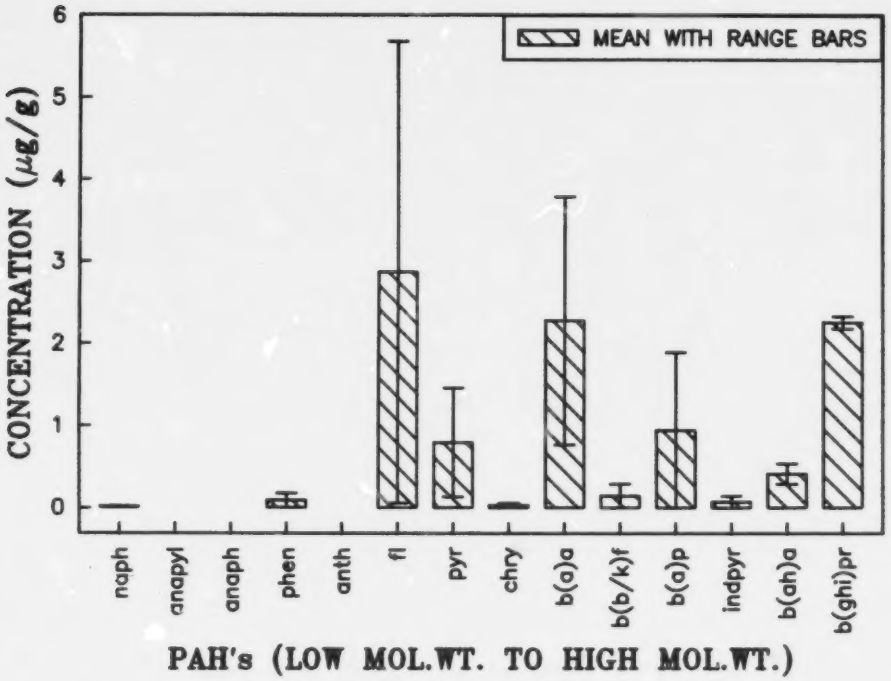


FIGURE 6.2.2.1.6 FINGERPRINT OF PAH'S IN SITE B TOPSOIL
BLOCKS 3 - MAY 1985

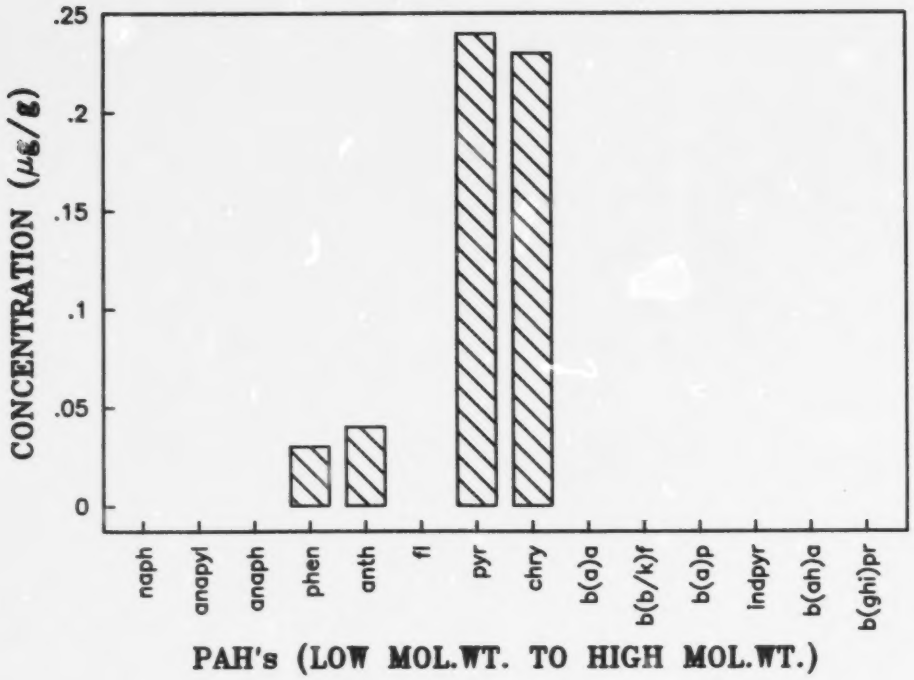


FIGURE 6.2.2.1.7 FINGERPRINT OF PAH'S IN SITE B TOPSOIL
BLOCKS 3 - JUNE 1985

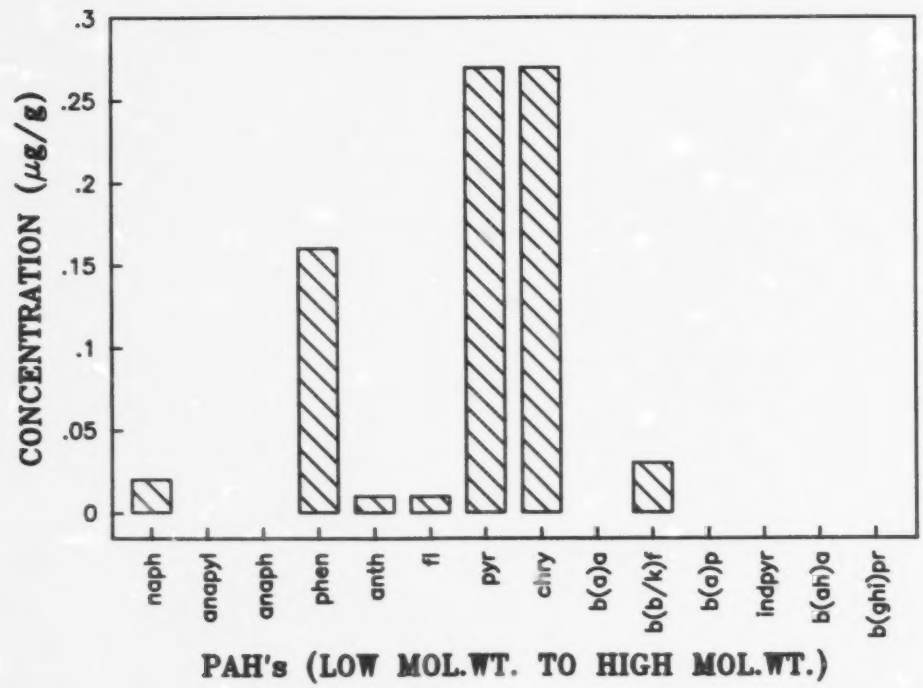


FIGURE 6.2.2.1.8 FINGERPRINT OF PAH'S IN SITE B TOPSOIL
BLOCKS 3 - JULY 1985

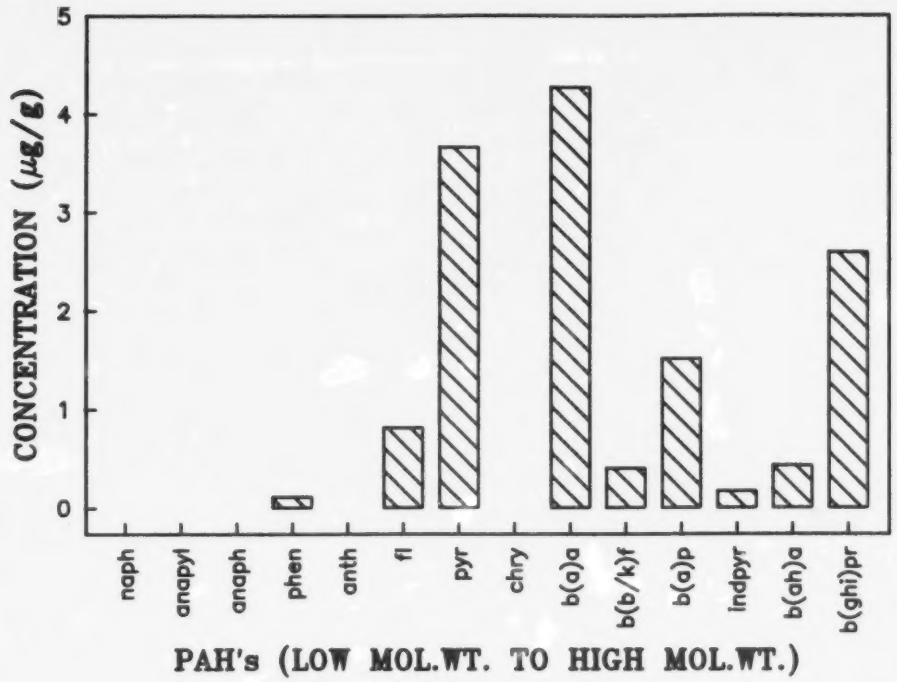


FIGURE 6.2.2.1.9 FINGERPRINT OF PAH'S IN SITE B TOPSOIL
BLOCKS 3 - AUGUST 1985

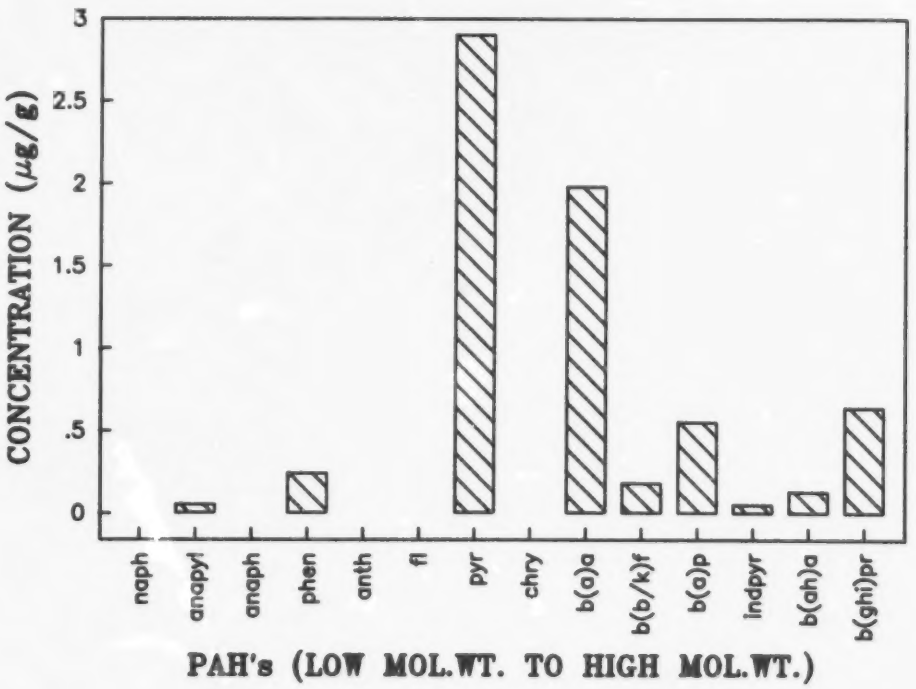


FIGURE 6.2.2.1.10 CONCENTRATION OF FLUORANTHENE IN SITE B TOPSOIL

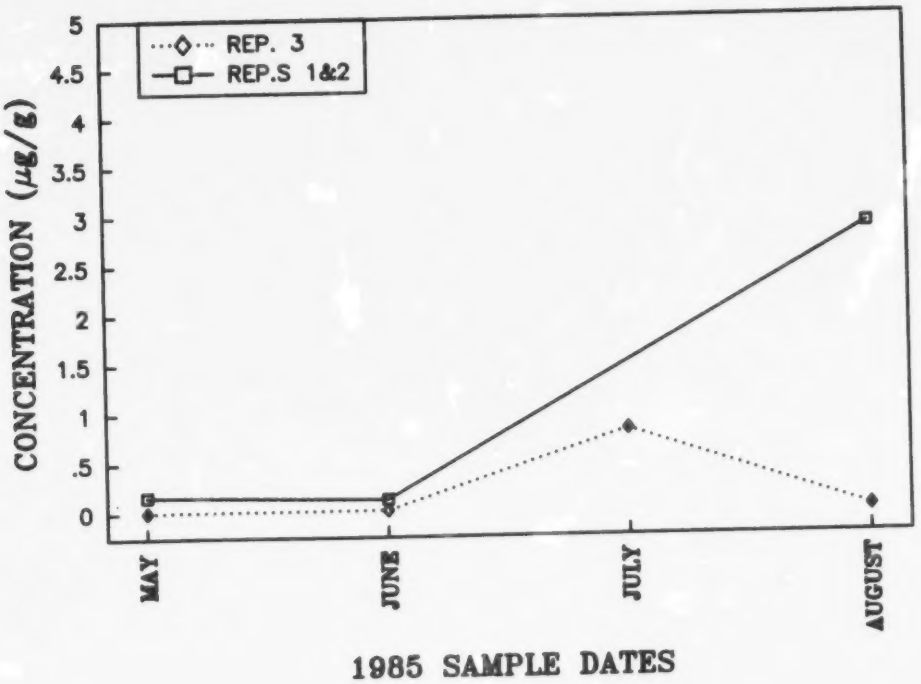


FIGURE 6.2.2.1.11 CONCENTRATION OF PYRENE IN SITE B TOPSOIL

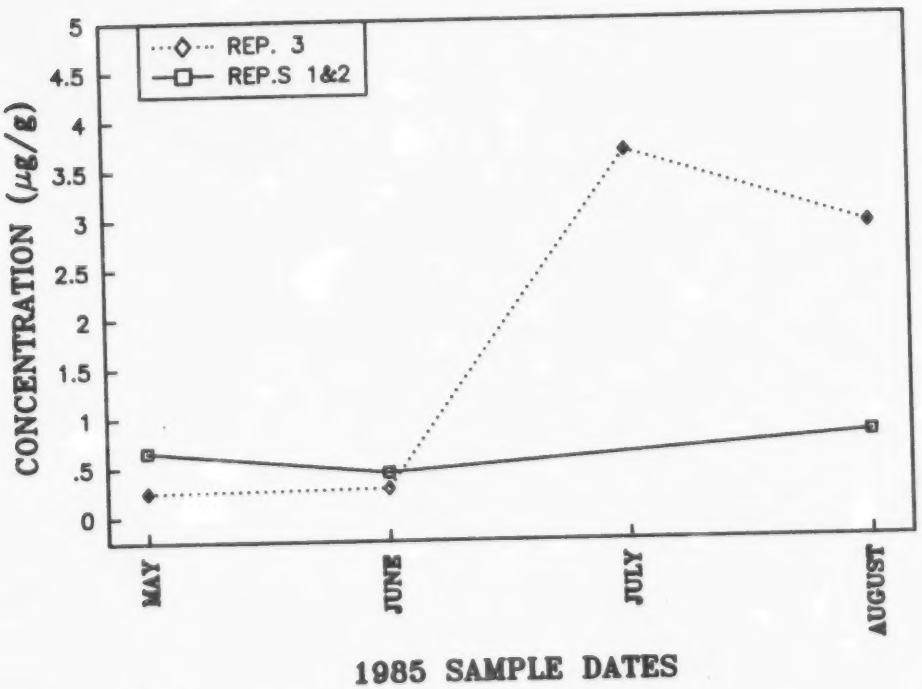


FIGURE 6.2.2.1.12 CONCENTRATION OF CHRYSENE IN SITE B TOPSOIL

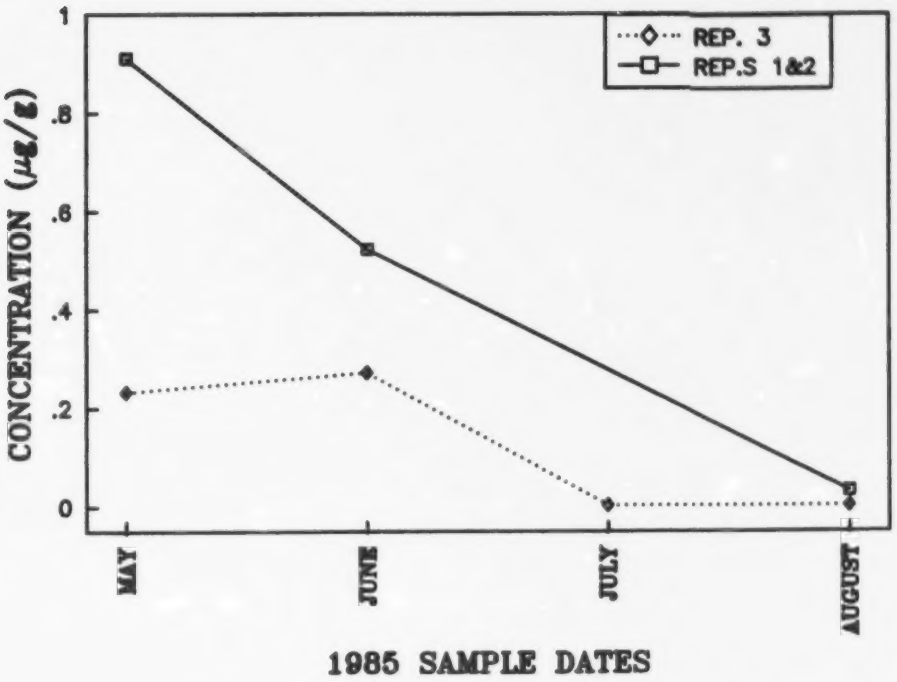


FIGURE 6.2.2.1.13 CONCENTRATION OF BENZO(A)ANTHRACENE IN SITE B TOPSOIL

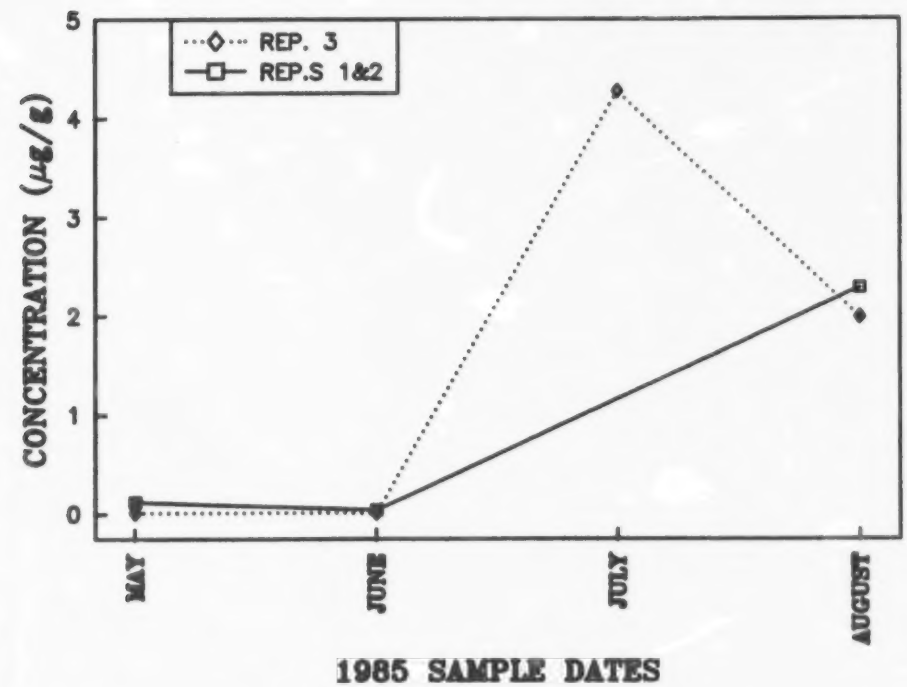


FIGURE 6.2.2.1.14 CONCENTRATION OF BENZO(A)PYRENE IN SITE B TOPSOIL

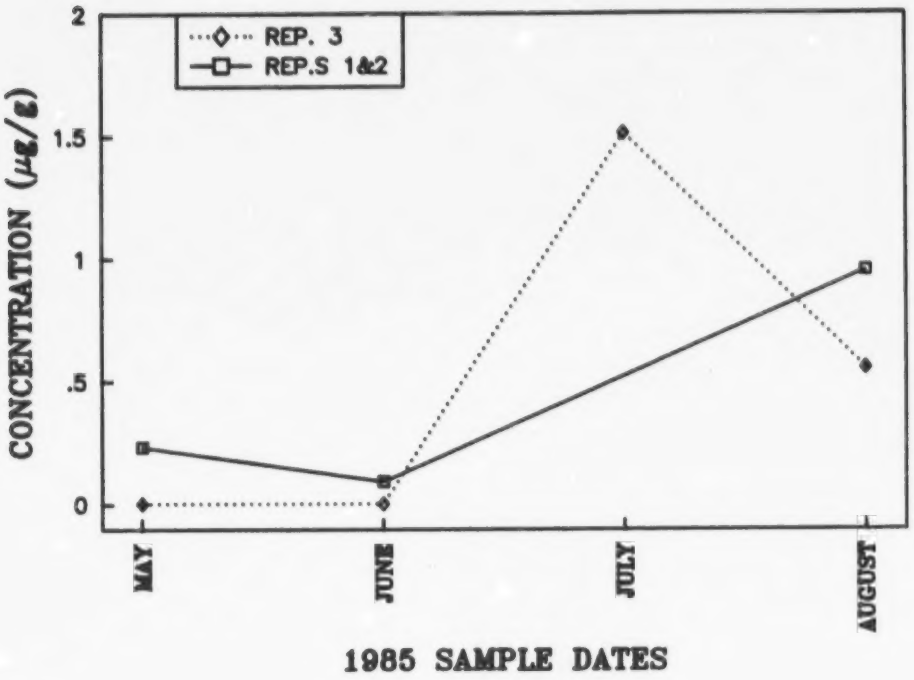


FIGURE 6.2.2.1.15 CONCENTRATION OF DIBENZO(A,H)ANTHRACENE IN SITE B TOPSOIL

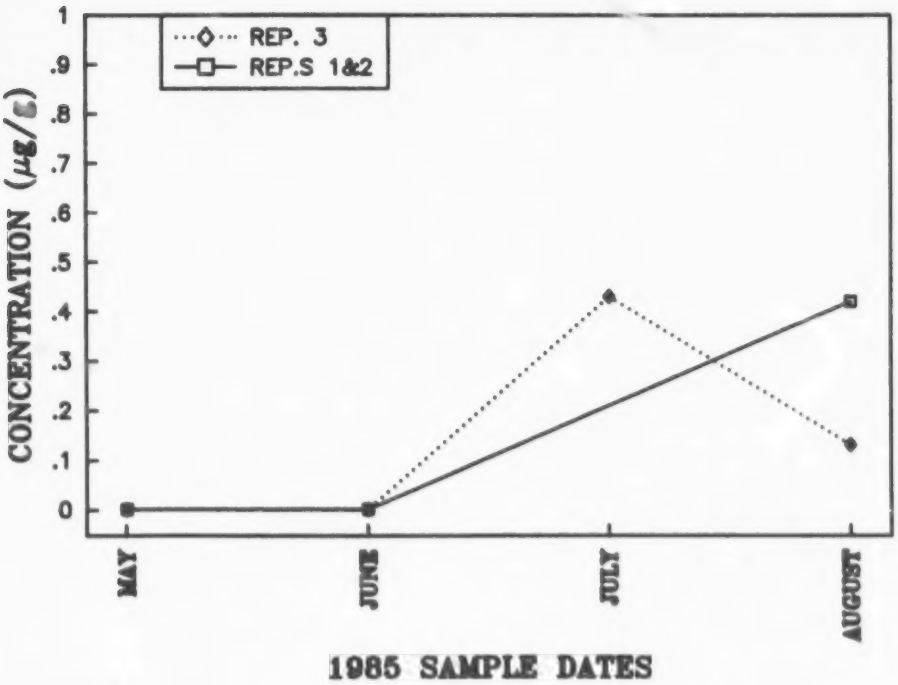


FIGURE 6.2.2.1.16 CONCENTRATION OF BENZO(G,H,I)PERYLENE IN SITE B TOPSOIL

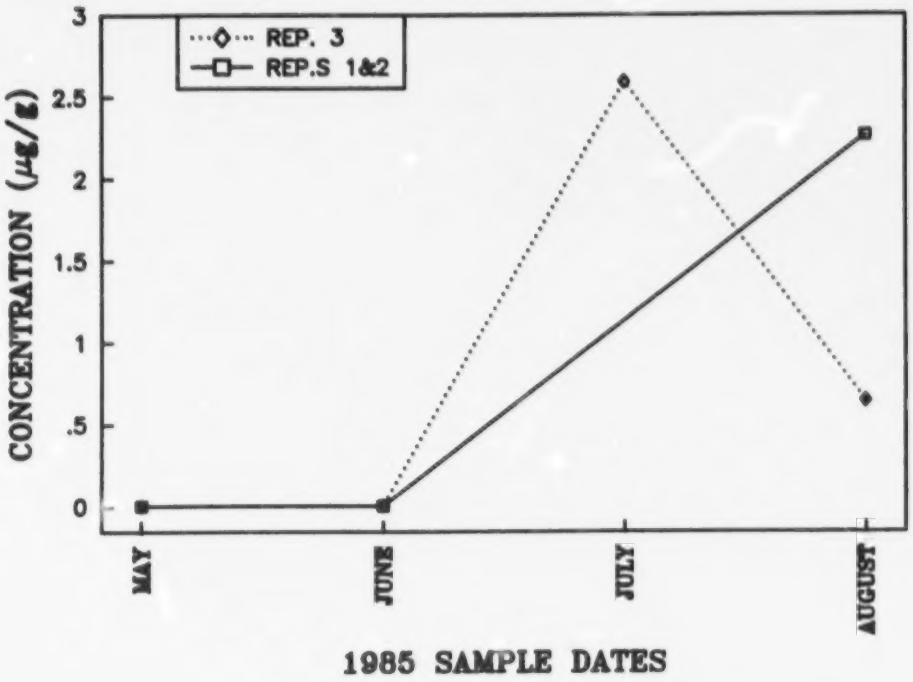


FIGURE 6.2.2.1.17 OIL IN SITE B LANDFARM TOPSOIL

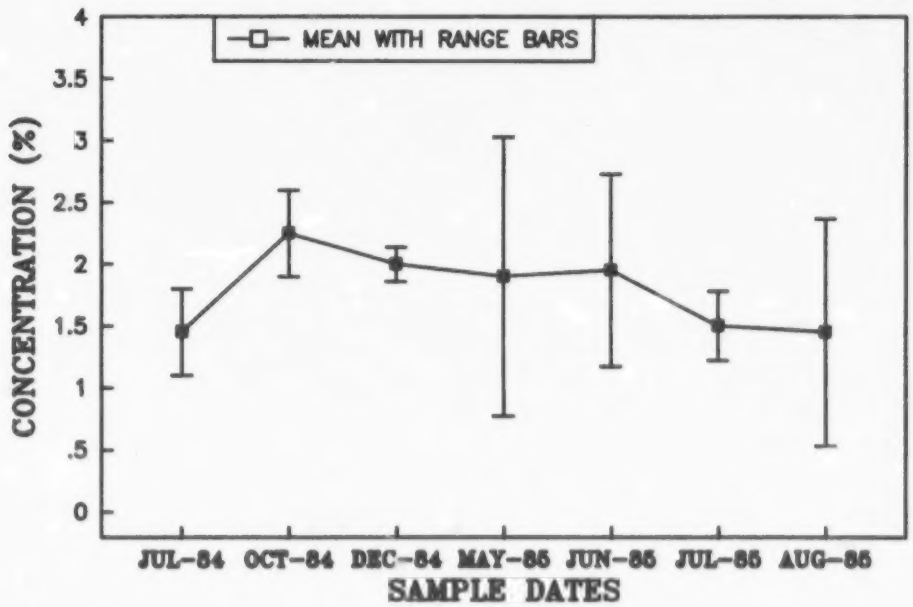


FIGURE 6.2.2.1.18 OIL VERSUS METALS CONTENT IN SITE B TOPSOIL

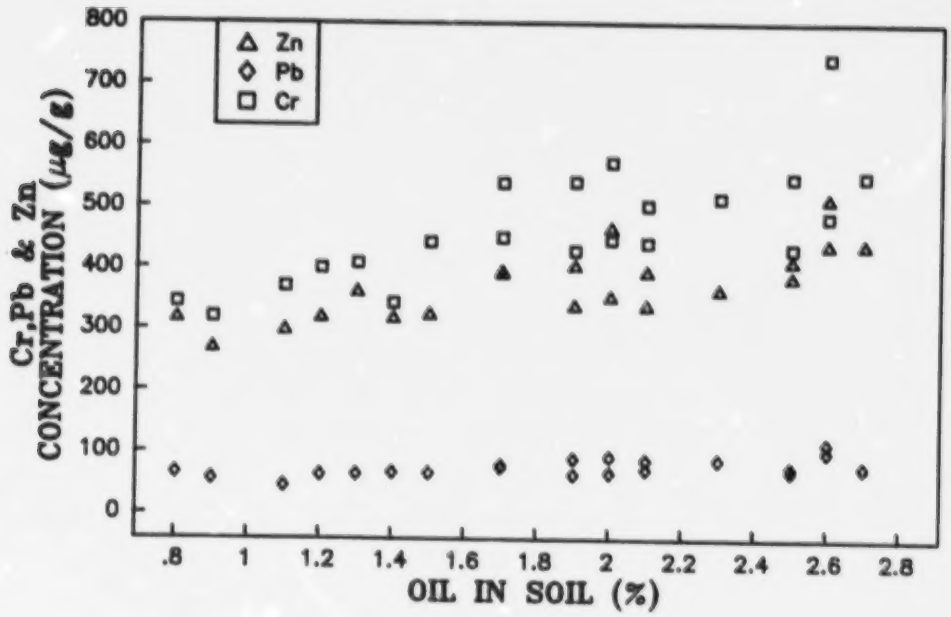


FIGURE 6.2.2.1.19 METALS VERSUS PAH CONTENT IN SITE B TOPSOIL

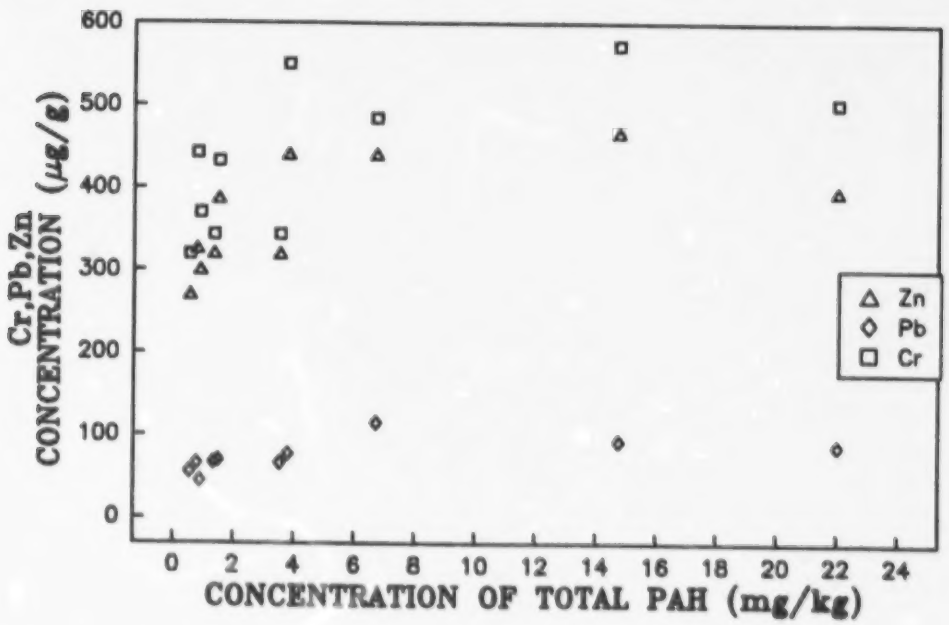


FIGURE 6.2.2.2.1 DOC IN WELLWATER (mg/L) SITE B - MAY 1985

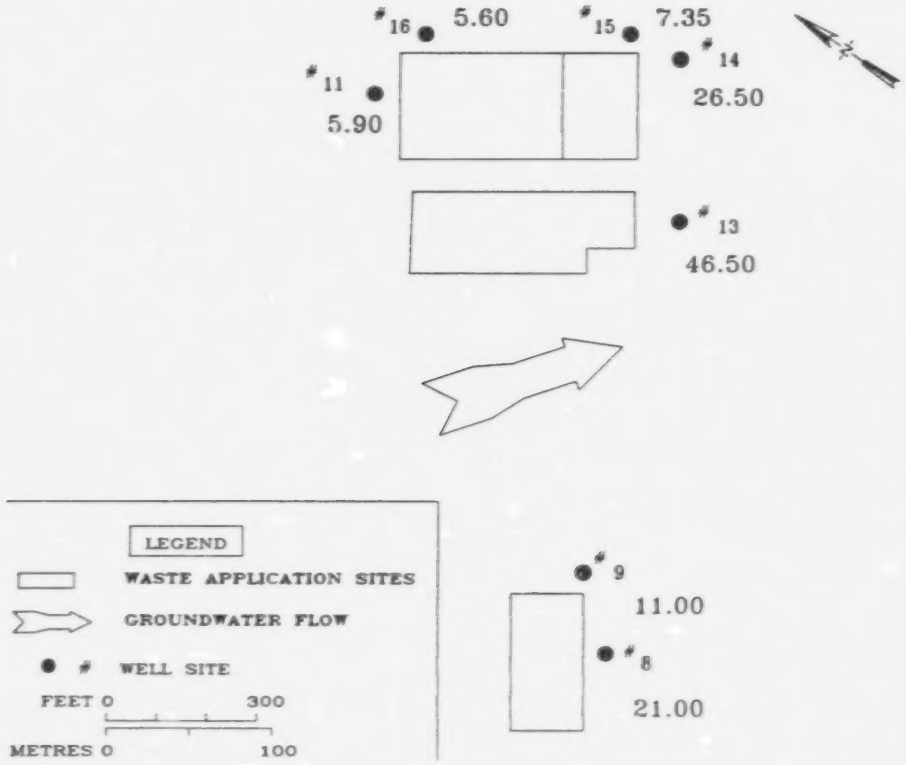


FIGURE 6.2.2.2.2 TOTAL PAH IN WELLWATER (µg/L) SITE B - MAY 1985

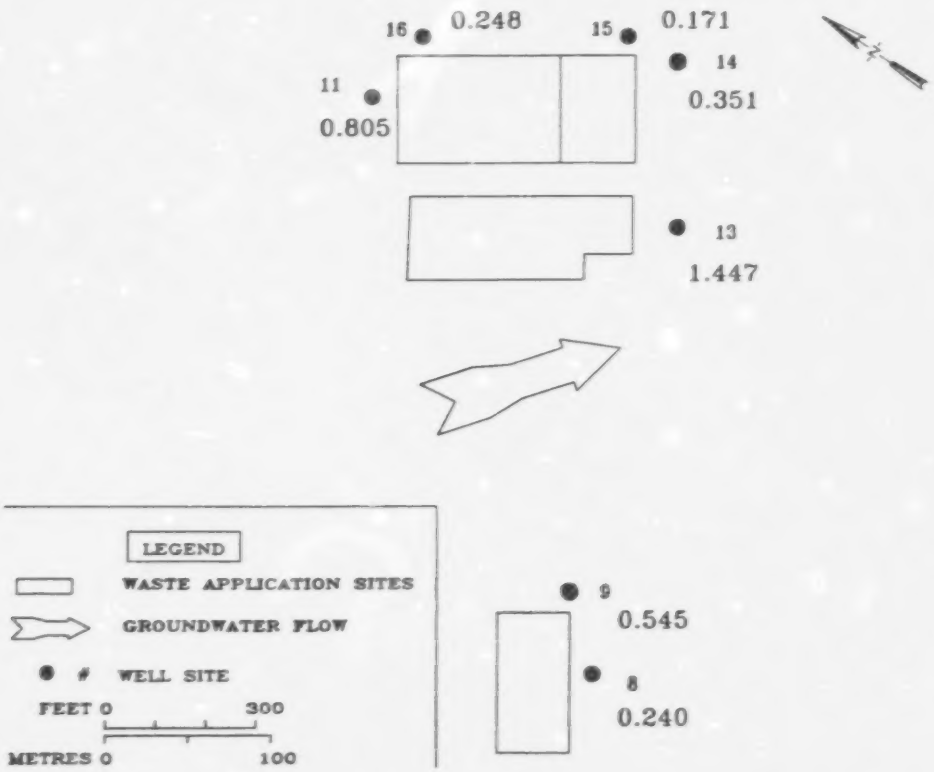


FIGURE 6.2.2.2.3 DOC IN WELLWATER (mg/L) SITE B - AUGUST 1985

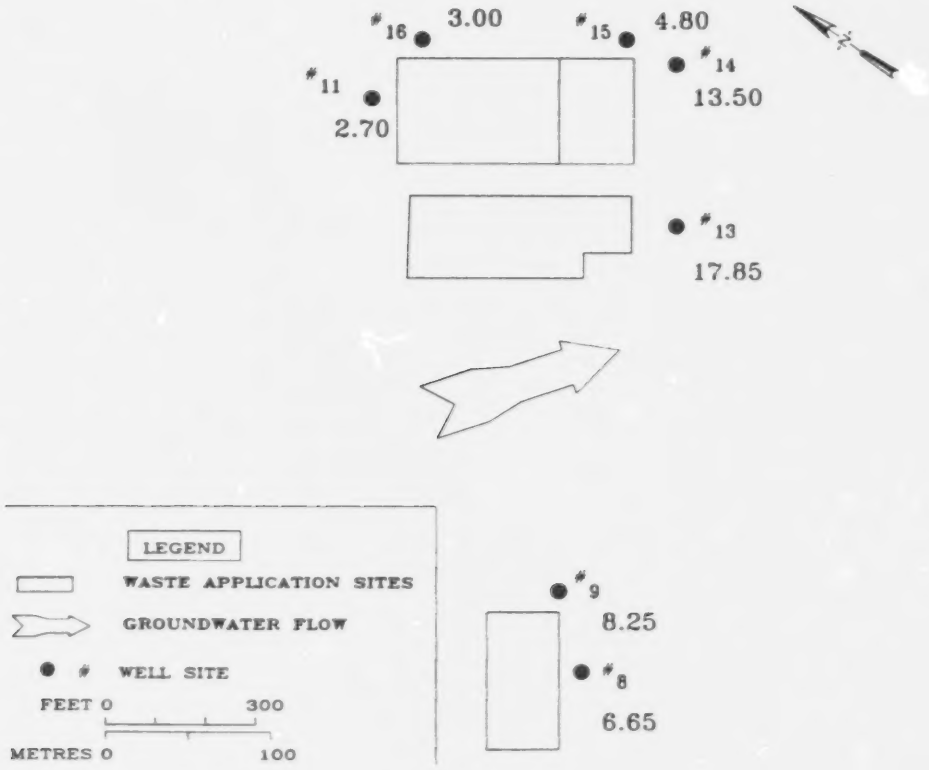


FIGURE 6.2.2.2.4 TOTAL PAH IN WELLWATER (µg/L) SITE B - AUGUST 1985

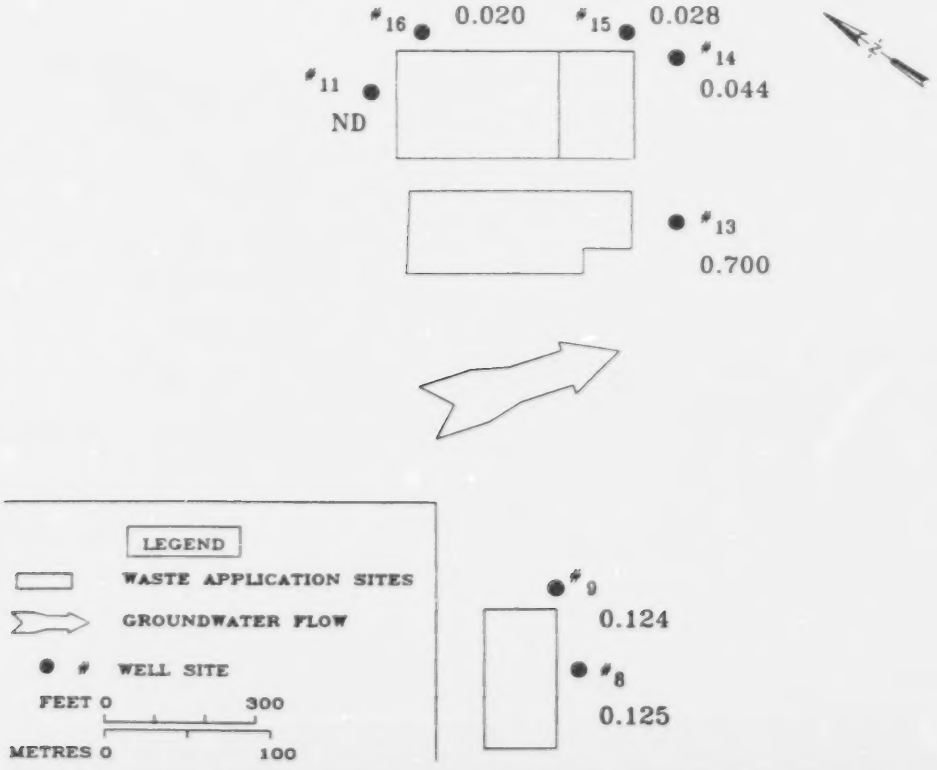


FIGURE 6.2.2.2.5 DOC IN SITE B WELLWATER - BACKGROUND WELLS

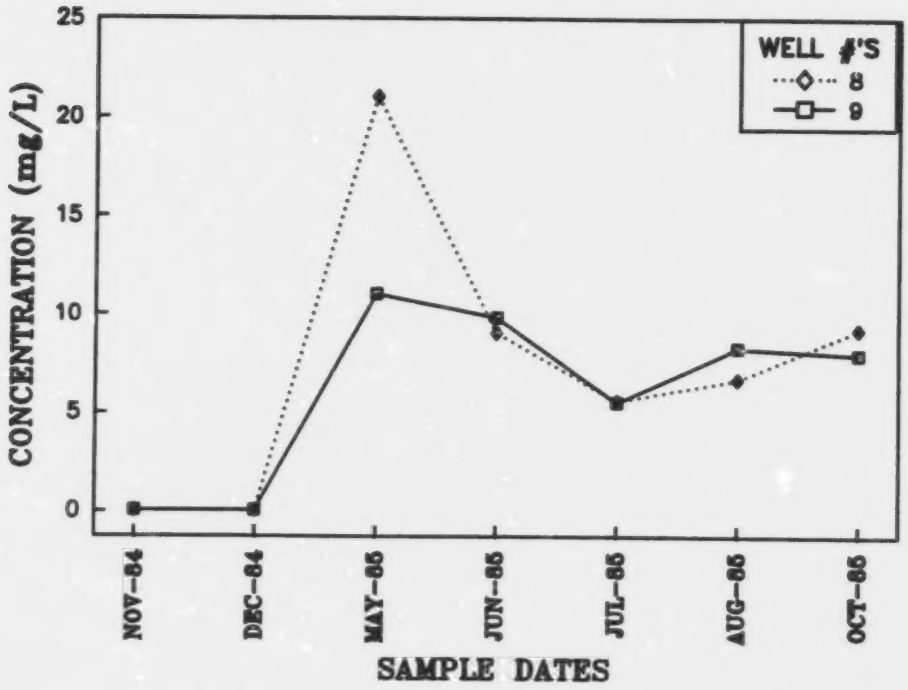


FIGURE 6.2.2.2.6 TOTAL PAH IN SITE B WELLWATER - BACKGROUND WELLS

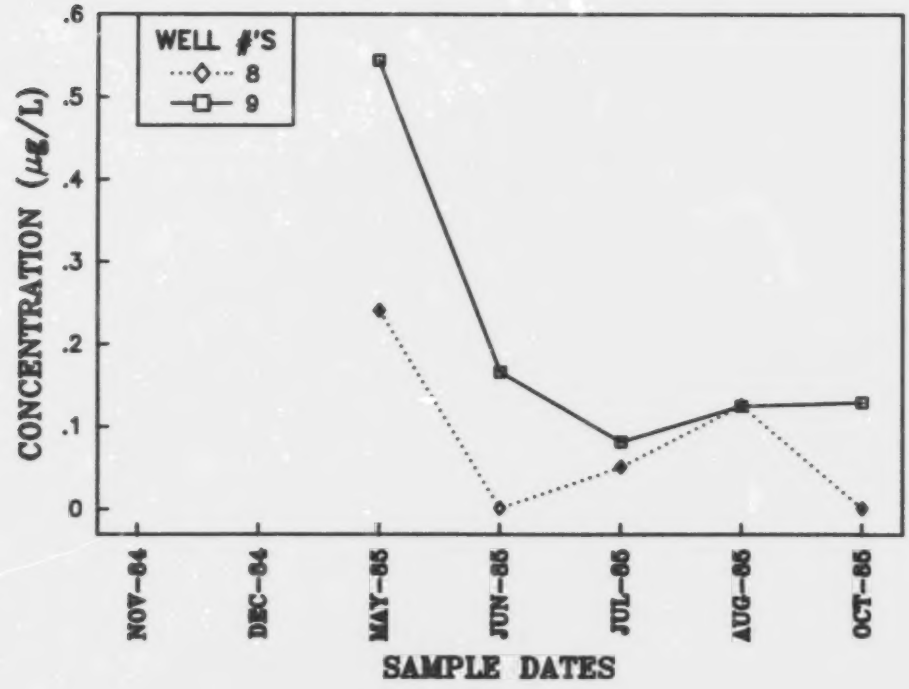


FIGURE 6.2.2.2.7 DOC IN SITE B WELLWATER - WELLS NEAR LANDFARM (NORTH AND WEST)

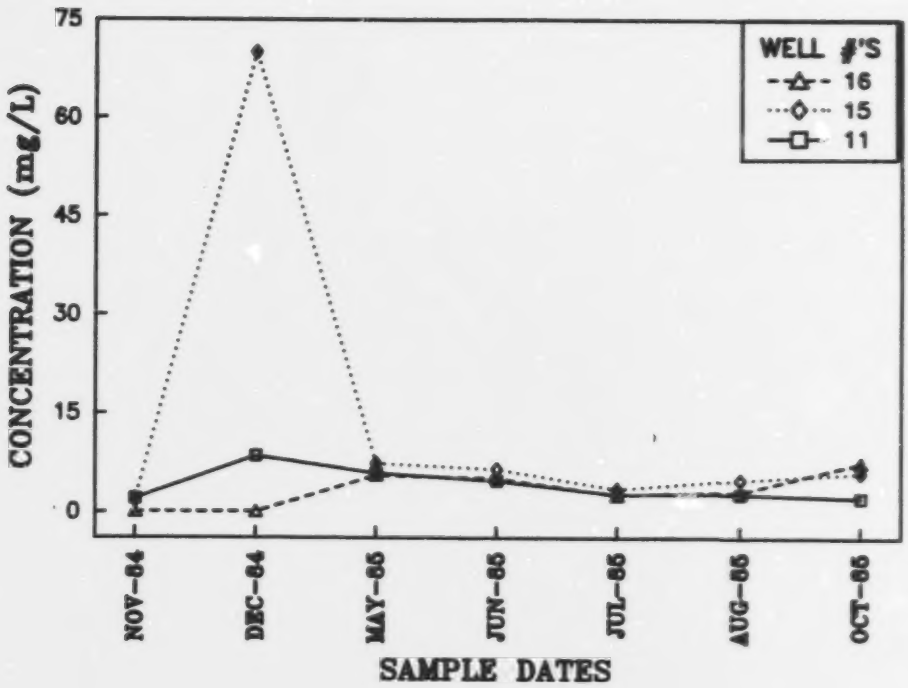


FIGURE 6.2.2.2.8 TOTAL PAH IN SITE B WELLWATER - WELLS NEAR LANDFARM (NORTH AND WEST)

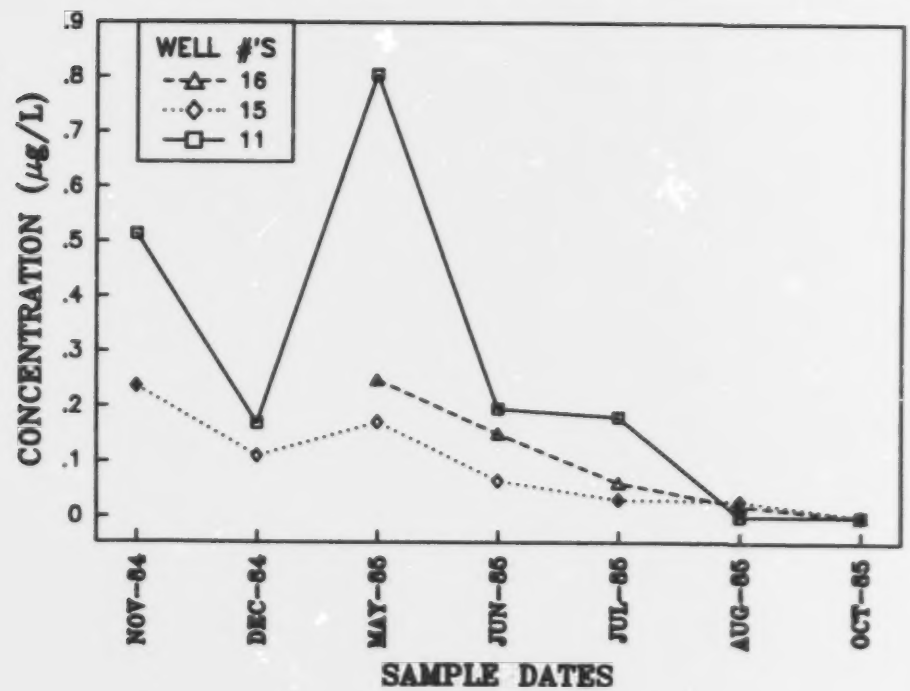


FIGURE 6.2.2.2.9 DOC IN SITE B WELLWATER - WELLS NEAR LANDFARM (EAST AND SOUTH)

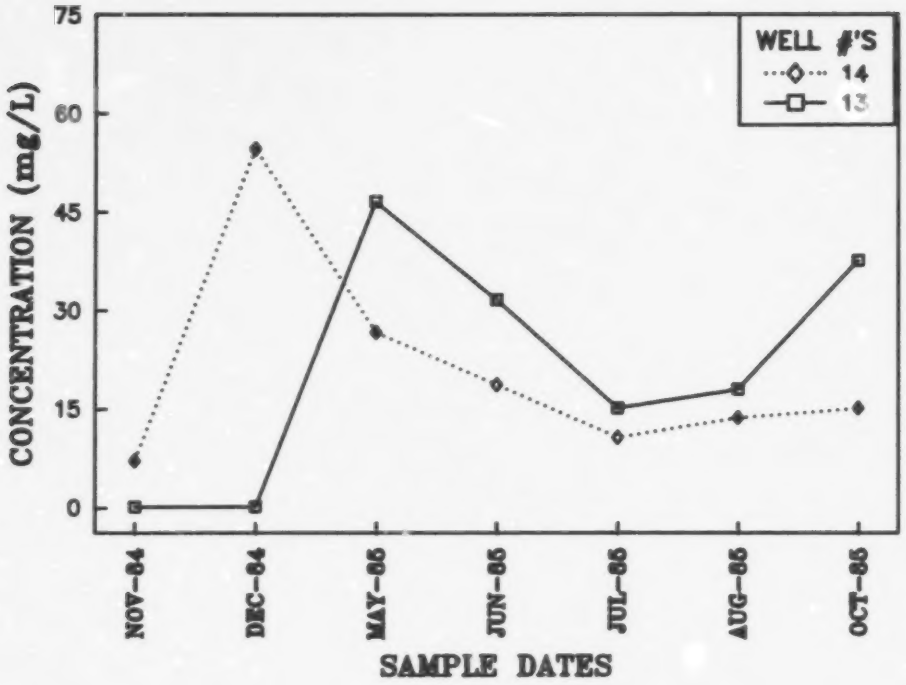


FIGURE 6.2.2.2.10 TOTAL PAH IN SITE B WELLWATER - WELLS NEAR LANDFARM (EAST AND SOUTH)

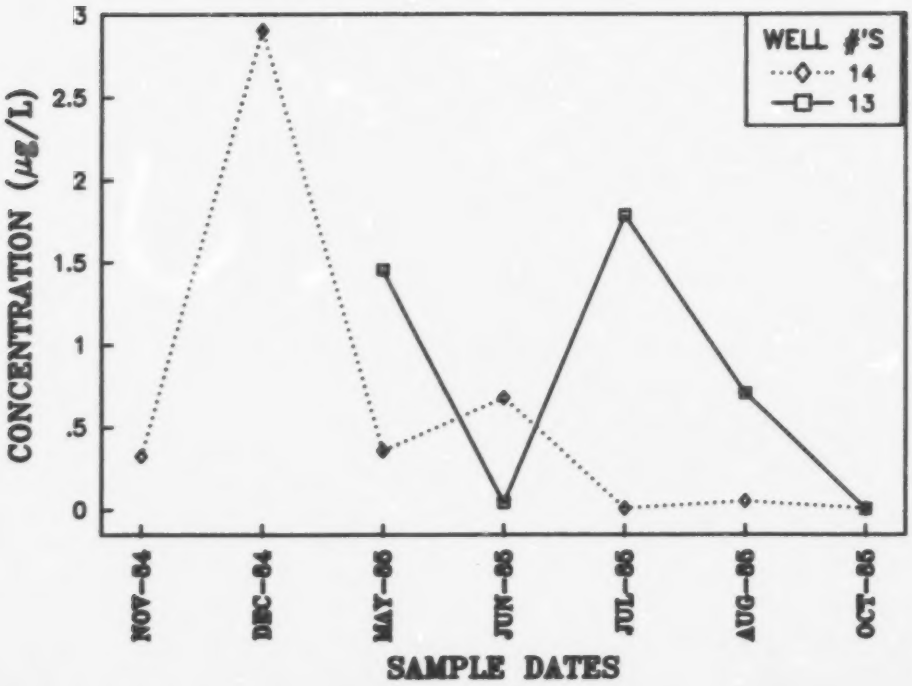


FIGURE 6.2.2.2.11 CONCENTRATION OF PHENANTHRENE IN SITE B WELLWATER NORTH AND WEST WELLS

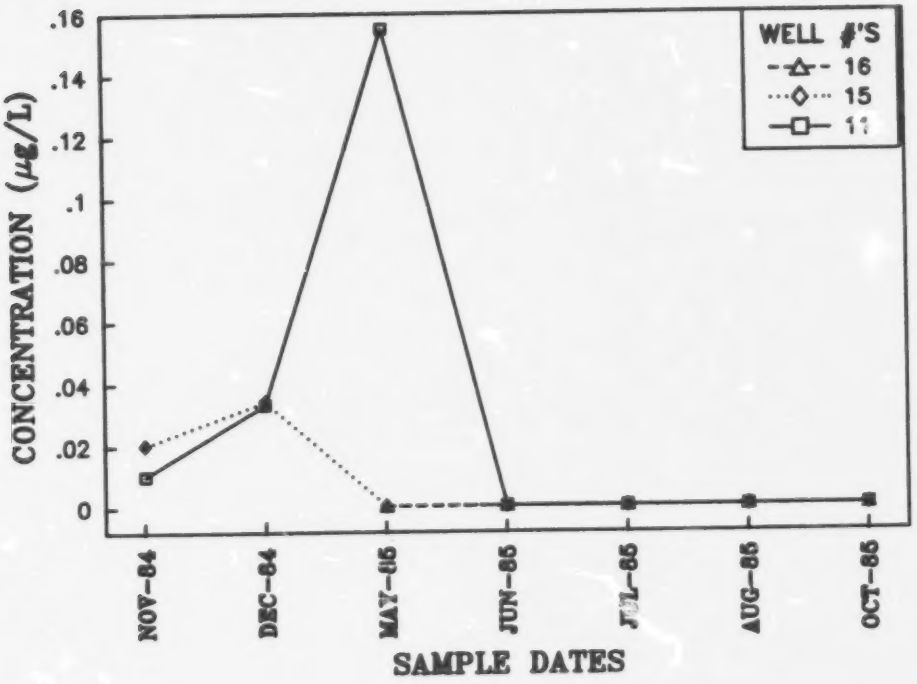


FIGURE 6.2.2.2.12 CONCENTRATION OF ANTHRACENE IN SITE B WELLWATER NORTH AND WEST WELLS

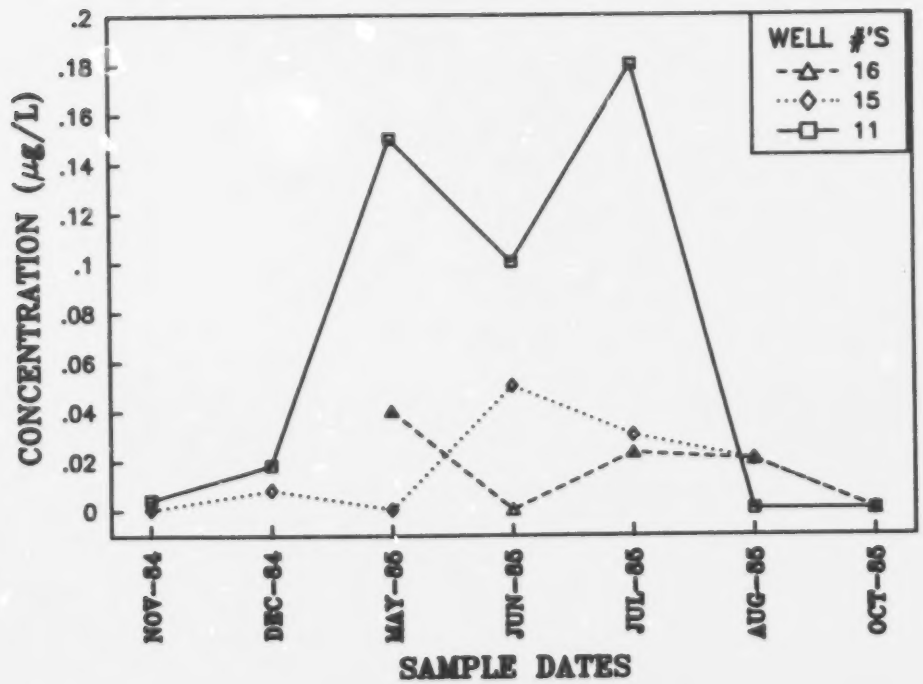


FIGURE 6.2.2.2.13 CONCENTRATION OF PYRENE IN SITE B WELLWATER
NORTH AND WEST WELLS

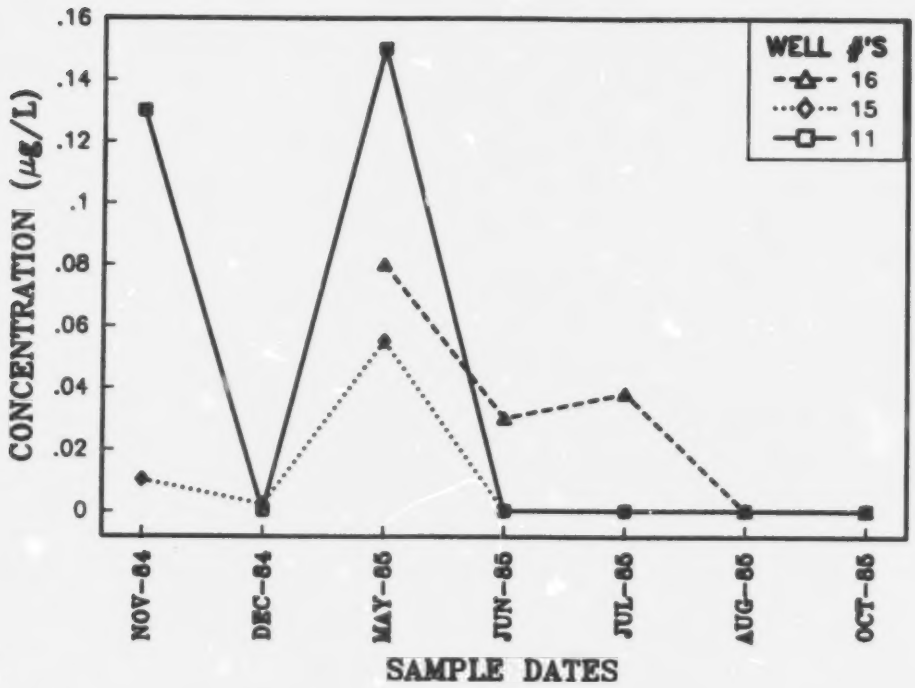


FIGURE 6.2.2.2.14 CONCENTRATION OF PHENANTHRENE IN SITE B WELLWATER
EAST AND SOUTH WELLS

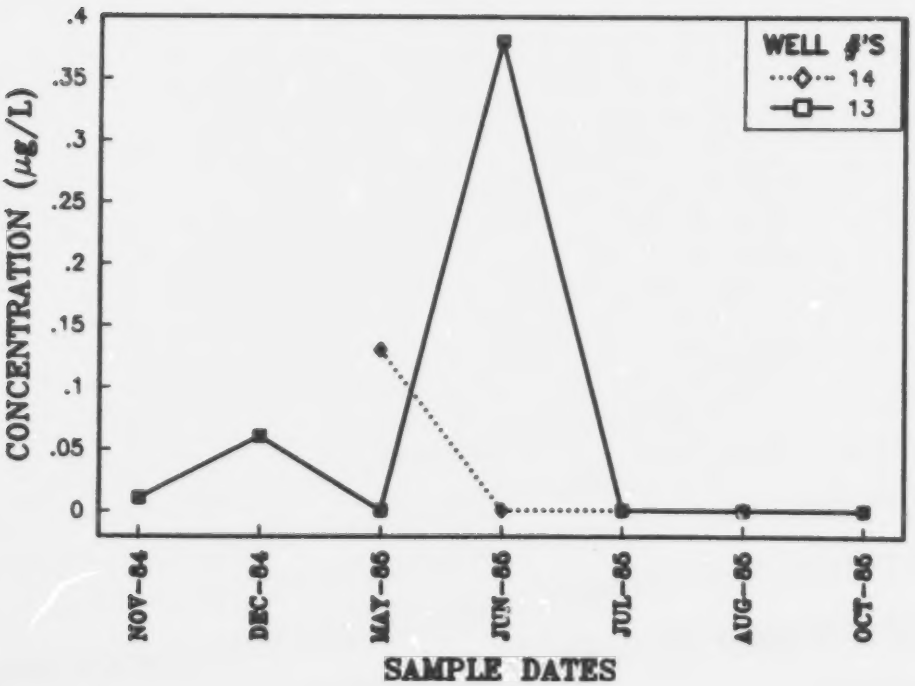


FIGURE 6.2.2.2.15 CONCENTRATION OF FLUORANTHENE IN SITE B WELLWATER EAST AND SOUTH WELLS

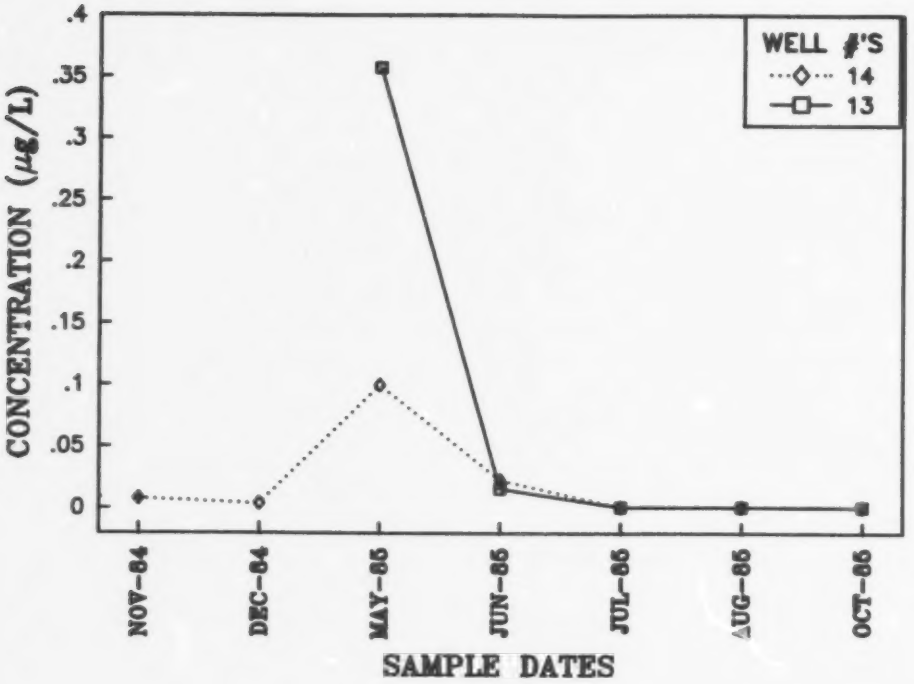
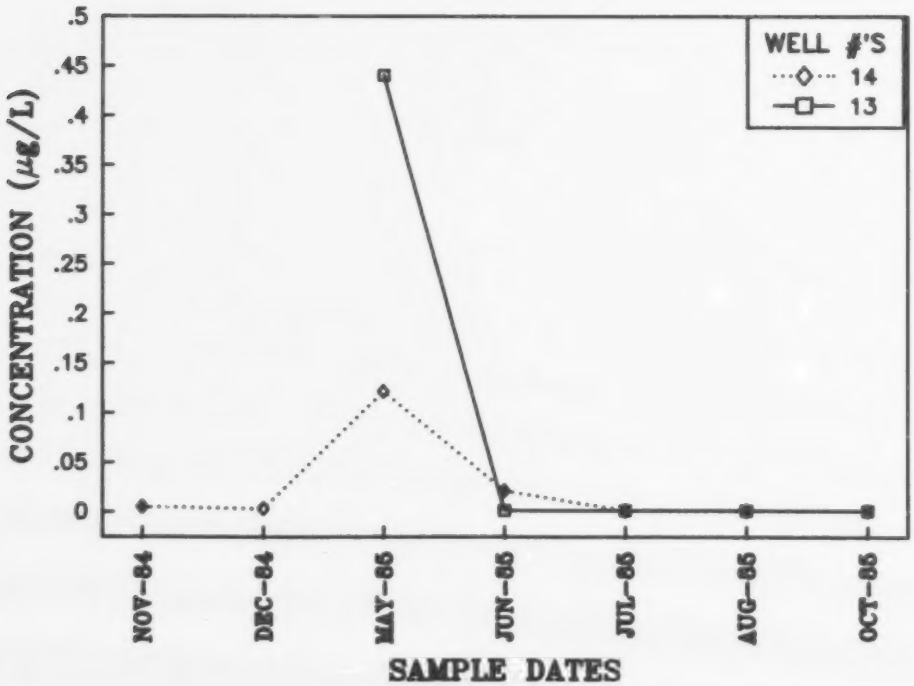


FIGURE 6.2.2.2.16 CONCENTRATION OF PYRENE IN SITE B WELLWATER EAST AND SOUTH WELLS



6.2.3 Landfarm Site C

Site C had been operated as a landfarm for a period of over 10 years prior to the study. It was located on a well drained, fine loamy sand. Heavy loadings of waste early in the site history, combined with intensive cultivation practices, had resulted in the development of a hard pan containing visible oil at a 6 to 15" depth, beneath a surface of well structured loamy sand. Recent landfarm practice had involved annual application of approximately 3% oil with intensive cultivation but no fertilizer addition.

6.2.3.1 Soil

Initial levels of oil, metals, basic cations and total target PAH in soil from Site C are presented in Table 6.2.3.1.1. A history of waste application to this site is evident from somewhat elevated levels of oil, metal and total PAH concentrations. Background lead and zinc concentrations are particularly high, possibly as a result of aerial deposition. Application of oily waste (460 m^3/ha) containing 13% oil (wet weight basis), took place in October of 1984.

Table 6.2.3.1.1 Initial concentrations of gross parameters and total target PAH in background and oily waste contaminated soil at site C.

		Background	Oily Waste Site
oil and grease	(%)	<0.01	2.77
Calcium	(%)	1.85	3.79
Potassium	(%)	1.65	1.12
Magnesium	(%)	0.54	0.60
Sodium	(%)	1.75	0.85
Cadmium	(mg/kg)	0.95	<0.5
Chromium	(mg/kg)	55	50
Lead	(mg/kg)	278	85
Zinc	(mg/kg)	213	161
pH		-	6.27
EC	(mS/cm^2)	-	1.70
Total PAH	(mg/kg)	0.2	6.50
CEC		1.6	19.2
sand (%)		-	73
silt (%)		-	22
clay (%)		-	5

The concentrations of individual PAH's in the waste applied to site C are presented in Table 6.2.3.1.2 and are similar to those for sites A and B. The initial level of total target PAH in soil was equivalent to that of about

1/20 the concentration of sludge. The total target PAH concentration and proportions of molecular weight groups in soil over the monitoring period are illustrated in Figure 6.2.3.1.1. Data for only one replicate was available for the June sampling period. It is curious that the total target PAH concentration appeared to increase in the July sampling period. It is likely, however, that this was due to sample variability and the effect, in early sample periods, of degradable organic chemicals interfering in analysis, particularly of the higher molecular weight constituents. The sludge constituents, illustrated at 1/10 concentration, were typically dominated by low molecular weight constituents. These components appear to have volatilized or degraded by the time soil was sampled, with chemicals in the 202 - 228 molecular weight range becoming dominant. The proportions of the molecular weight groups in soil appeared to remain relatively constant over the monitoring period, although the absolute concentrations varied.

Table 6.2.3.1.2 Concentration of PAH's in sludge from site C

PAH	molecular weight	Concentration (mg/kg dry weight)
naphthalene	128	13.82
acenaphthylene	152	3.88
acenaphthene	154	17.11
phenanthrene	178	92.11
anthracene	178	3.55
fluoranthene	202	1.45
pyrene	202	7.24
chrysene	228	5.00
benzo(a)anthracene	228	0.19
benzo(b)fluoranthene/ benzo(k)fluoranthene	252	ND
benzo(a)pyrene	252	ND
indeno(1,2,3-c,d)pyrene	276	ND
dibenzo(a,h)anthracene	278	ND
benzo(g,h,i)perylene	276	ND

ND: not detected (below 0.08 mg/kg for each PAH)

Individual fingerprint diagrams are illustrated in Figures 6.2.3.1.2-5 indicating the mean and range of PAH concentrations for three replicates (with the exception of the June period for which only one sample was available). Background PAH concentrations ranged up to 0.2 mg/kg. Concentrations of phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were observed to exceed background levels. It is difficult to attribute the elevated levels of all of these PAH's to a single preceding sludge application, as the levels of many of these PAH's were not detectable in the sludge. Two possibilities may explain the levels of these PAH's in soil. The concentrations of some of these PAH's in sludge or in early soil samples may be masked by interfering compounds, and therefore the estimate of PAH additions and original concentrations in

soil may not be precise. These PAH's may also have accumulated in soil over many years of waste application. As there is no direct evidence that PAH's of the 202 - 278 molecular weight range decreased in soil over the monitoring period, it seems plausible that some accumulation might occur. It is likely that the high PAH concentrations in soil resulted from both the latest sludge addition and the accumulation of PAH's over time.

Several PAH's appeared to increase in concentration over the monitoring period. Data for the July sampling period was extremely variable for many PAH's, however, there was a trend of increasing concentration between May and August sampling periods (i.e. the range of concentrations for those periods do not overlap). Plots of concentration over the monitoring period for those PAH's which exceeded background concentrations are presented in Figures 6.2.3.1.6 - 13. The means and ranges of concentrations for three replicates are illustrated. The concentration of chrysene appears to have decreased over the monitoring period, while those of fluoranthene, pyrene and benzo(g,h,i)perylene appear to have increased substantially. The concentrations of benzo(a)anthracene, benzo(b/k)fluoranthene and benzo-(a)pyrene may have increased slightly. The data for dibenzo(a,h)anthracene is too variable to draw any conclusion. Due to sample variability and the limited number of samples taken, the data was not suitable for kinetic modelling. Variability in the samples was typically high and is discussed in Appendix B.

The oil content in site C soil increased substantially following waste addition in 1984 and mean oil content declined by approximately 1% (from 6% to 5% oil and grease) over the monitoring period. Sample variability was high and no significant difference in oil content was observed over time. Figure 6.2.3.1.14 illustrates the concentration of oil in the soil. Discussions with refinery personnel revealed that, in previous years, degradation rates of approximately 3% oil and grease per year were achieved with annual additions of about 3% oil. As a loss of 1% rather than 3% was observed, the efficiency of the waste application area appeared to be below normal over the monitoring period for this study and may not be typical of the site in general. Annual variations in environmental conditions or failure to meet the nutrient demands of the soil may have led to a reduction in biodegradation efficiency for the oil. This would likely have an impact on the fate of constituent PAH's as well.

Table 6.2.3.1.3 Final concentrations of gross parameters and total target PAH in oily waste contaminated soil at site C.

oil and grease	(%)	5.24
Calcium	(%)	4.20
Potassium	(%)	1.41
Magnesium	(%)	0.69
Sodium	(%)	1.00
Cadmium	(mg/kg)	<0.5
Chromium	(mg/kg)	93.67
Lead	(mg/kg)	111.0
Zinc	(mg/kg)	275
pH		7.15
EC	(mS/cm^2)	1.20
Total target PAH	(mg/kg)	20.35

The concentration of chromium and zinc increased with the waste addition in 1984. The concentrations of chromium, zinc and lead in soil were somewhat related to the oil content of soil, with a distinct relationship evident between oil and zinc. The concentrations of chromium, zinc and lead in soil are compared to that of oil in Figure 6.2.3.1.15. No relationship between oil and total target PAH concentrations or metal and total target PAH concentrations was observed.

Table 6.2.3.1.3 summarizes the final concentrations of gross parameters and total target PAH in the waste treated soil at the end of the monitoring period. Oil, metals and total target PAH content all appeared to have increased in soil over the monitoring period.

6.2.3.2 Groundwater

Sampling of groundwater at Site C began with 9 wells in September and December of 1984 and continued with an additional 7 wells to October 1985. Initial monitoring revealed that the two wells positioned upstream from the waste application site, for collection of background samples (wells 1 and 2), were directly contaminated with processed diesel fuel. This rendered the wells useless for background monitoring purposes. Sampling of wells 1 and 2 continued, to assess the impact of their contamination on the rest of the site. Two additional upstream wells (4 and 5) and several wells farther downstream were added to the sampling program to provide assessment of background concentrations. As sampling proceeded in September and December of 1984 beginning with wells 1 and 2, it is likely that some contamination of subsequent samples occurred. Data from the two initial sampling periods is therefore considered less reliable than data from later sampling periods.

Figures 6.2.3.2.1 and 6.2.3.2.2 illustrate the concentrations of dissolved organic carbon (DOC) and total target PAH, respectively, in samples collected from wells throughout the site in May 1985, with the exception of wells 1, 2 and 10. Analysis of PAH's in these wells was unsuccessful in May 1985, due to interference from other organic compounds in the UV spectral range. For these three wells, data is provided from the September 1984 sampling period. The direction of groundwater flow is from west to east, according to an unpublished consultants' report.

Inspection of Figure 6.2.3.2.1 indicates that a plume of organically loaded groundwater existed in the region of the waste application area, however, the orientation of the plume is not clear, due to insufficient sampling points. The DOC content in wells 1 and 2 reflects the diesel fuel contamination of these wells. As oil was removed prior to DOC analysis, however, only the dissolved fraction of the diesel fuel has been quantified. Well 1 was slotted over a 1.4 to 3 m depth (depth to static water table was 2 m) whereas well 2 was slotted to a 6.7 m depth.

Of the two background wells sampled in May (wells 4 and 5), only well 5 provided enough sample for both PAH and DOC analysis, thus only one DOC value is reported. Well 4 was slotted over a 0.6 to 1.8 m depth (depth to static water table was 1.1 m), whereas well 5 was slotted to 5.5 m depth.

Background DOC values in the range of 4.7 to 13.0 mg/L were observed in all downstream wells at a distance greater than 70 m from the active waste

application areas. One well within 70 m of the waste application area, but slotted over a depth of 5 to 8 m, also contained DOC levels in the background range. Other wells near the waste application area were slotted from near the surface (0.5 m) to a depth of up to 6 m. This distribution of DOC values suggests that organic loading of groundwater from the waste application area was restricted to a zone within 70 m of the waste application site and to depth of less than 5 m. A detailed analysis of an organic plume beneath the waste application area was, however, beyond the scope of this study.

Total target PAH values in samples from the same period generally concur with the DOC values. Background levels of total target PAH ranged up to 0.36 µg/L. Total PAH concentrations, which exceeded background levels, occurred in samples with high DOC and in the 70 m zone next to the waste application site, as well as in those from the diesel contaminated wells. Two exceptions were noted. Wells 13 and 14, which were placed at distances of approximately 130 and 200 m from the waste application area, contained elevated concentrations of PAH. Upon further discussion with refinery staff, it was learned that these wells are in close proximity to a main sewage trunk line. Well 13 had intersected the trunk line at 4.6 m upon installation. Well 13A had subsequently been installed to a depth of 7.5 m and approximately 20 m upstream from the trunk line. Well 14 was installed beside the trunk line to a depth of 7.2 m.

Figures 6.2.3.2.3 and 6.2.3.2.4 provide similar information for DOC and total PAH concentrations in wells sampled toward the end of the monitoring period. As many wells provided insufficient sample for DOC analysis in October, 1985, values from the August sampling period have been presented. The DOC values are similar to those found in the May sampling period. Total PAH concentrations had generally dropped to below the detection limits for most wells, as observed at sites A and B. These results suggest that the flux of PAH from surface soil and within groundwater had changed over the summer season, either in response to changes in water flux or microbial activity. Wells 13 and 14 were again exceptions, with total target PAH concentrations similar to those found in May, suggesting that the source of PAH's was consistent over the monitoring period.

The preceding figures provide a basis for grouping the wells into general categories, as follows: wells 1 and 2 = diesel contaminated wells, wells 4, 5, 6, 13A, 15 and 16 = background wells, wells 7 and 10 = wells near landfarm (significantly contaminated), wells 8, 9, 11 and 12 = wells near landfarm (slightly contaminated) and possibly affected by waste applications, wells 13 and 14 = wells likely affected by the proximity of a sewage trunk line. This grouping is supported by a comparison of the individual PAH's and PAH molecular weight groups found in these samples. To simplify the presentation of results, each group will be discussed separately beginning with the least contaminated group and progressing to the groups showing the most contamination.

Background wells contained total PAH concentrations ranging from not detected to 0.44 µg/L over the monitoring period, with peak total PAH generally in the May/June period and corresponding to high DOC. Figures 6.2.3.2.5 and 6.2.3.2.6 illustrate the concentrations of DOC and total target PAH, respectively, in background wells over the monitoring period. A typical profile of PAH molecular weight groups in background wells is

illustrated in Figure 6.2.3.2.7, for well 15. PAH's in the 128-178 molecular weight range were generally absent. The proportions of PAH in the 202-228, 252 and 276-278 molecular weight ranges were generally similar. Concentrations of these molecular weight groups were approximately 0.1 µg/L in May and June and not detected thereafter.

The concentrations of DOC and total target PAH in wells 8, 9, 11 and 12 (near the landfarm and slightly contaminated) are illustrated in Figures 6.2.3.2.8 and 6.2.3.2.9, respectively, for the entire monitoring period.

The concentration of total target PAH in well 9 did not exceed that of background wells throughout the monitoring period, however the concentration was highest in September of 1984 and dropped through the May/June period, as did the concentrations in wells 8 and 12. Furthermore, the proportions of PAH molecular weight groups were similar in these three wells. Figure 6.2.3.2.10 illustrates the profile of PAH molecular weight groups in well 12, which is typical of that in these slightly contaminated wells. The PAH's in the 128-178 molecular weight range predominated in these wells in September and December 1984 (0.1 - 0.8 µg/L). The higher molecular weight PAH's predominated in early 1985 (0.1 µg/L or less) and by late 1985 there were no PAH's detected. The concentrations of individual PAH's in these wells followed a similar trend with time as those of total PAH (Figure 6.2.3.2.8), peaking in September, December or May and decreasing to below detection by the end of the monitoring period. Individual PAH's exceeding background (0.1 µg/L) in well 8 included acenaphthene (0.39 µg/L), anthracene (0.14 µg/L), chrysene (0.12 µg/L) and dibenzo(a,h)anthracene (0.19 µg/L). Individual PAH's exceeding background in well 12 included acenaphthene (0.8 µg/L), chrysene (0.12 µg/L) and dibenzo(a,h)anthracene (0.11 µg/L). Figures 6.2.3.2.11 and 6.2.3.2.12 illustrate the concentrations of chrysene and dibenzo(a,h)anthracene, respectively, in wells 8, 9, 11 and 12.

Well 11 was somewhat different from other wells in the slightly contaminated group in that the concentrations were greatest in July and the PAH's were predominantly in the 252 and 276-278 molecular weight range. Individual PAH's exceeded background concentrations in July only and included benzo(b)fluoranthene (0.17 µg/L), benzo(k)fluoranthene (0.13 µg/L), benzo(a)pyrene (0.19 µg/L) and benzo(g,h,i)perylene (0.19 µg/L). The concentration of many PAH's, including these four, also appeared to peak in waste treated soil in July. Figures 6.2.3.2.13 and 6.2.3.2.14 illustrate the concentrations of benzo(a)pyrene and benzo(g,h,i)perylene, respectively, in wells 8, 9, 11 and 12. The concentrations of several PAH's in well 11 appear to follow a trend similar to that observed in waste treated soil over the same period. The reason for differences between wells near the waste application area is not clear.

Wells 13 and 14, near the sewage trunk line, showed evidence of PAH contamination predominated by high molecular weight PAH's throughout the monitoring period. The concentrations of total PAH and DOC for the monitoring period are illustrated in Figures 6.2.3.2.15 and 6.2.3.2.16, respectively. The total and individual PAH concentrations were generally bimodal, with a peak in December or the following May and another peak in July or August. The proportions of PAH molecular weight groups were similar to those found in background wells, but at much higher concentrations (0.2-2.0 µg/L 202-228 molecular weight, 0.2-2.5 µg/L 252

molecular weight and 0.15-0.8 µg/L 276-278 molecular weight). The profile of PAH molecular weight groups is illustrated in Figure 6.2.3.2.17 for samples from well 13. Individual PAH's which exceeded background levels in wells 13 and 14, respectively, included fluoranthene (0.12 and 0.75 µg/L), pyrene (0.13 and 0.79 µg/L), benzo(a)anthracene (0.16 and 0.58 µg/L), benzo(b)fluoranthene (0.16 and 1.4 µg/L), benzo(k)fluoranthene (0.06 and 0.3 µg/L), chrysene (0.17 and 0.27 µg/L), dibenzo(a,h)anthracene (0.39 and 0.33 µg/L), indeno(1,2,3-c,d)pyrene (0.2 and 0.17 µg/L) and benzo-(g,h,i)perylene (0.19 and 0.67 mg/L). The concentrations of chrysene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene, respectively, for wells 13 and 14 over the entire monitoring period are illustrated in Figures 6.2.3.2.18 to 6.2.3.2.21.

The most severely contaminated wells included wells 7 and 10, near the landfarm, and those contaminated directly with diesel fuel (wells 1 and 2). Most of the high PAH concentrations in wells 7 and 10 occurred in September and December of 1984 and may have resulted from cross contamination with wells containing diesel fuel. Additional difficulties were incurred with samples taken from these wells in May and June of 1985, as they contained high levels of UV adsorbing organic material which interfered with PAH analysis. As a result, data for several PAH compounds is missing for these periods. The DOC and total target PAH and concentrations for wells 1, 2, 7 and 10 over the monitoring period are illustrated in Figures 6.2.3.2.22 and 6.2.3.2.23. Total PAH concentrations for wells 7 and 10 were low in the later 1985 sample periods, although the DOC concentrations remained high. The samples from wells 1 and 2 contained PAH's predominantly in the 128-154 molecular weight group, as might be expected from a refined product such as diesel fuel. Samples from wells 7 and 10 also contained predominantly low molecular weight PAH's, similar to wells 1 and 2 and in contrast to other wells near the waste application site (8 and 11). The profile of PAH molecular weight groups in wells 1 and 7 are illustrated in Figures 6.2.3.2.24 and 6.2.3.2.25, respectively. It appears likely that the abundance of low molecular PAH in wells 7 and 10 came from wells 1 and 2 early in the monitoring period and are not representative of contamination resulting from waste application to soil.

Detection limits of PAH's in groundwater varied with the PAH and are provided in Appendix B.

It was apparent that contamination of groundwater in the vicinity of the landfarm area came from a number of sources, including a sewage trunk line and direct exposure of well water to a contaminating fluid. The proportions of PAH's, constituting a "fingerprint" of contamination, were useful for comparing the PAH loadings from the possible sources of contamination. For example, high molecular weight PAH were present in greater concentrations than low molecular weight PAH's in background wells and wells near the sewage trunk line (the ratios of 252-278 g mol^{-1} to 128-178 g mol^{-1} were in the range 5 to 72), although wells near the sewage trunk line contained much higher concentrations than background wells. Wells contaminated directly with diesel fuel had the highest PAH concentrations of all wells and contained predominantly low molecular weight PAH's (ratios of high to low molecular weight PAH's ranged from 0.03 to 0.13). Wells near the landfarm contained a greater proportion of high molecular weight PAH's (ratios of high to low molecular weight PAH's ranging from 0.33 to 4.5) than

those contaminated with diesel fuel. In addition, PAH's were not detected in wells near the landfarm in the latter part of the monitoring period, whereas elevated levels were detected in wells near the sewage line throughout the monitoring period. This comparison suggested that the landfarm activities did make a distinct contribution to PAH loadings in groundwater adjacent to the landfarm during a portion of the year. Higher concentrations of PAH's in groundwater occurred next to the sewage trunk line, however, which was downstream from the landfarm site.

FIGURE 6.2.3.1.1 PROPORTION OF PAH'S IN SITE C LANDFARM TOPSOIL GROUPED BY MOLECULAR WEIGHT

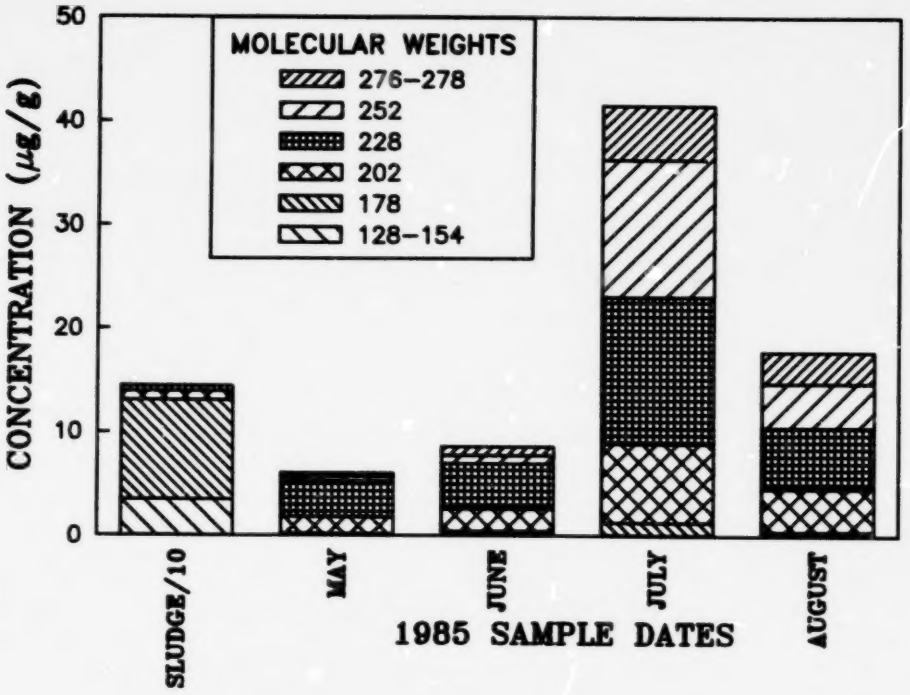


FIGURE 6.2.3.1.2 FINGERPRINT OF PAH'S IN SITE C TOPSOIL
MAY 1985

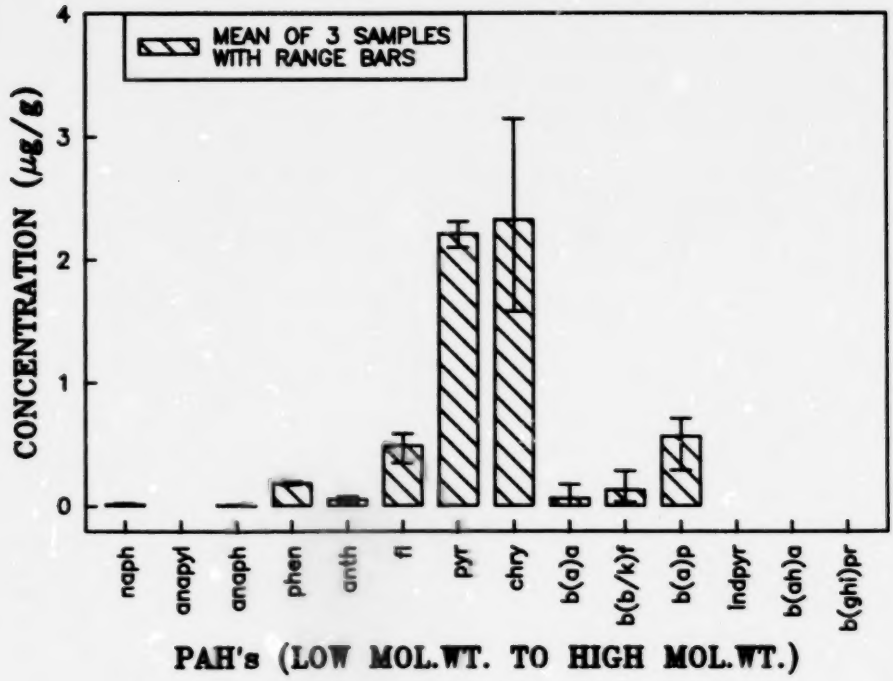


FIGURE 6.2.3.1.3 FINGERPRINT OF PAH'S IN SITE C TOPSOIL
JUNE 1985

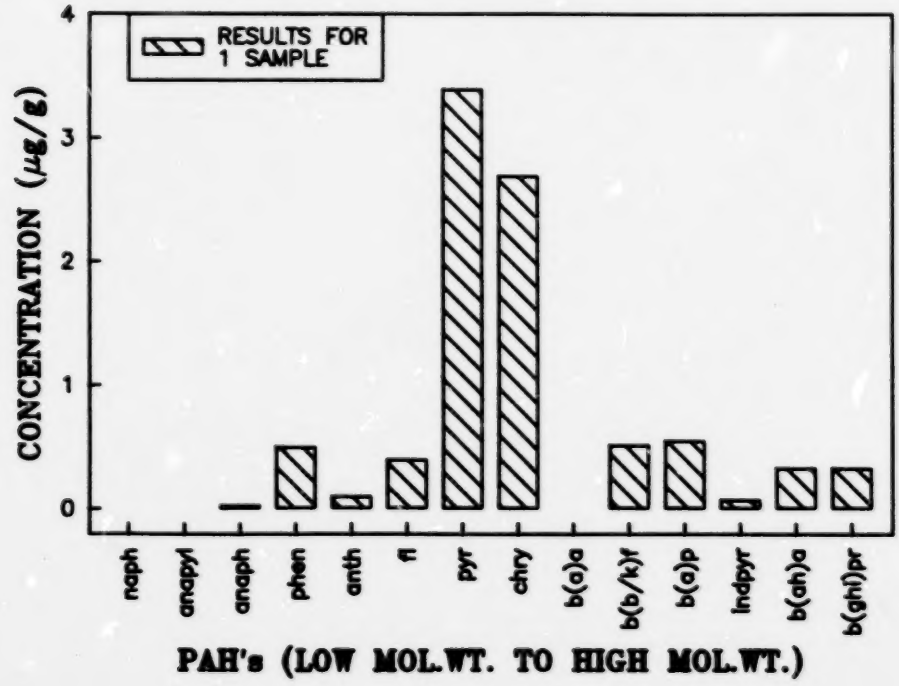


FIGURE 6.2.3.1.4 FINGERPRINT OF PAH'S IN SITE C TOPSOIL
JULY 1985

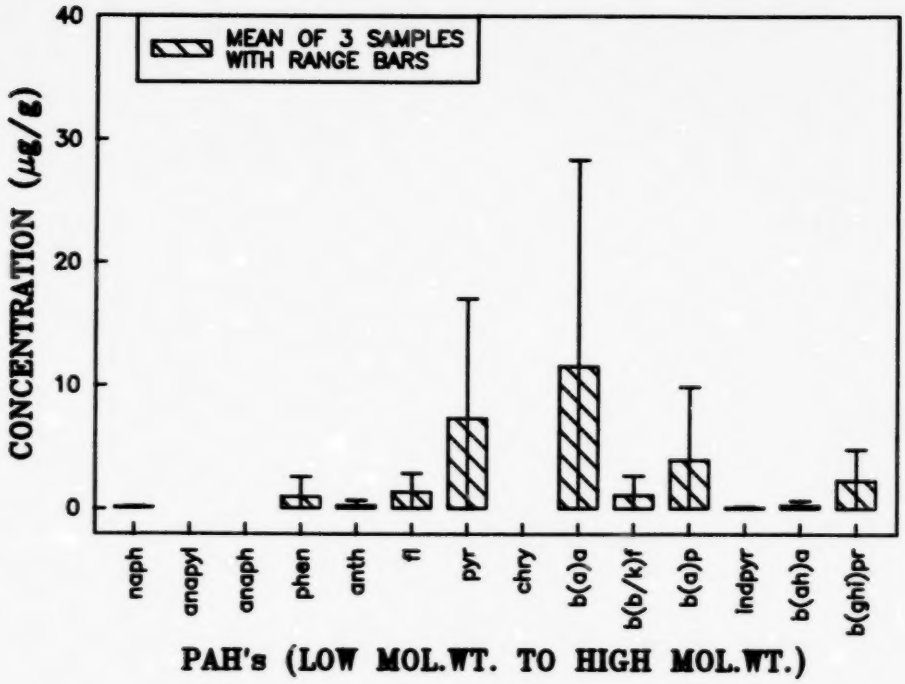


FIGURE 6.2.3.1.5 FINGERPRINT OF PAH'S IN SITE C TOPSOIL
AUGUST 1985

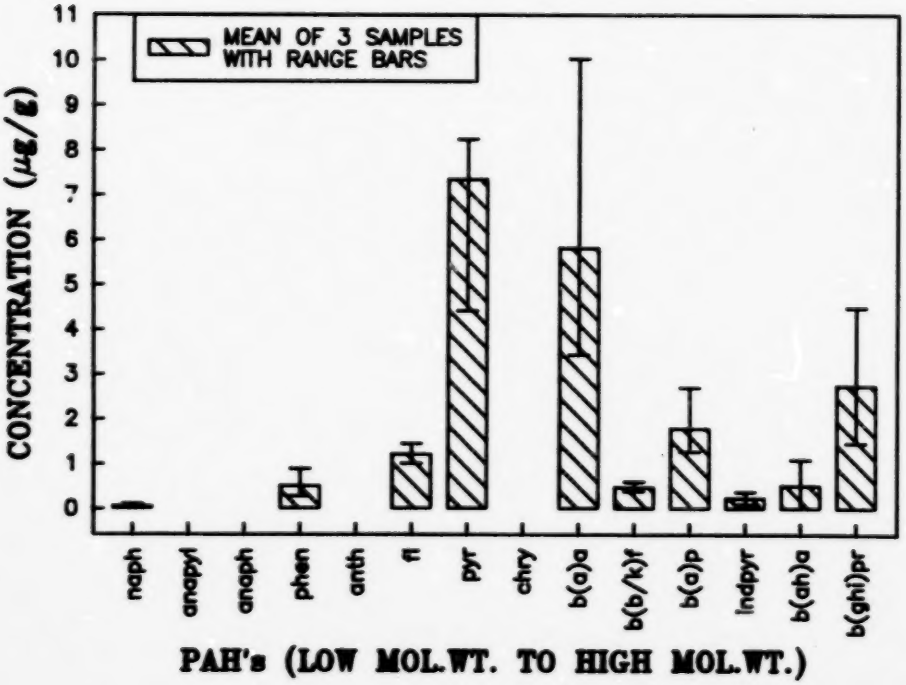


FIGURE 6.2.3.1.6 CONCENTRATION OF FLUORANTHENE IN SITE C TOPSOIL

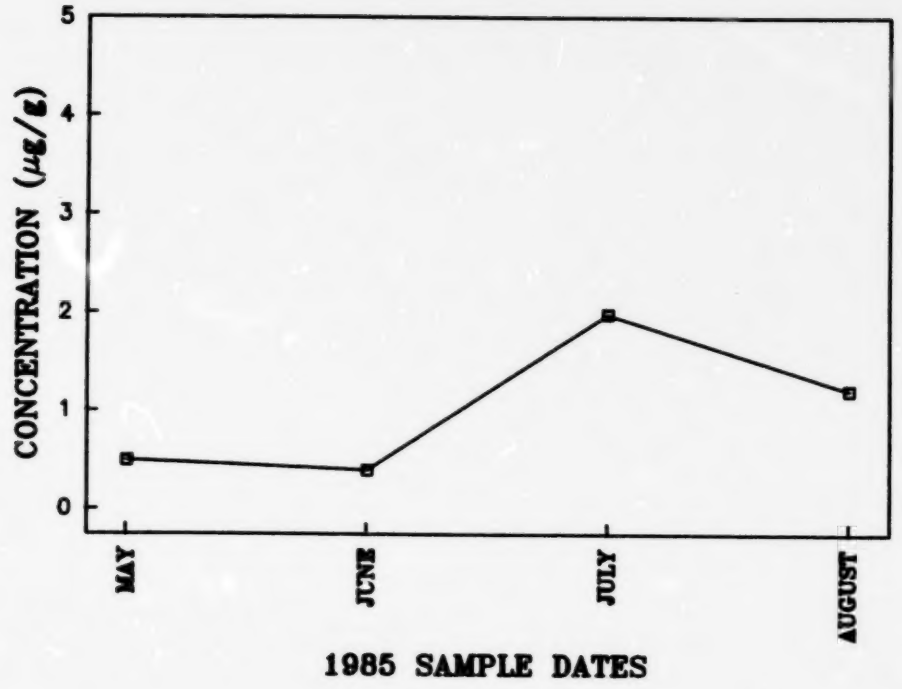


FIGURE 6.2.3.1.7 CONCENTRATION OF PYRENE IN SITE C TOPSOIL

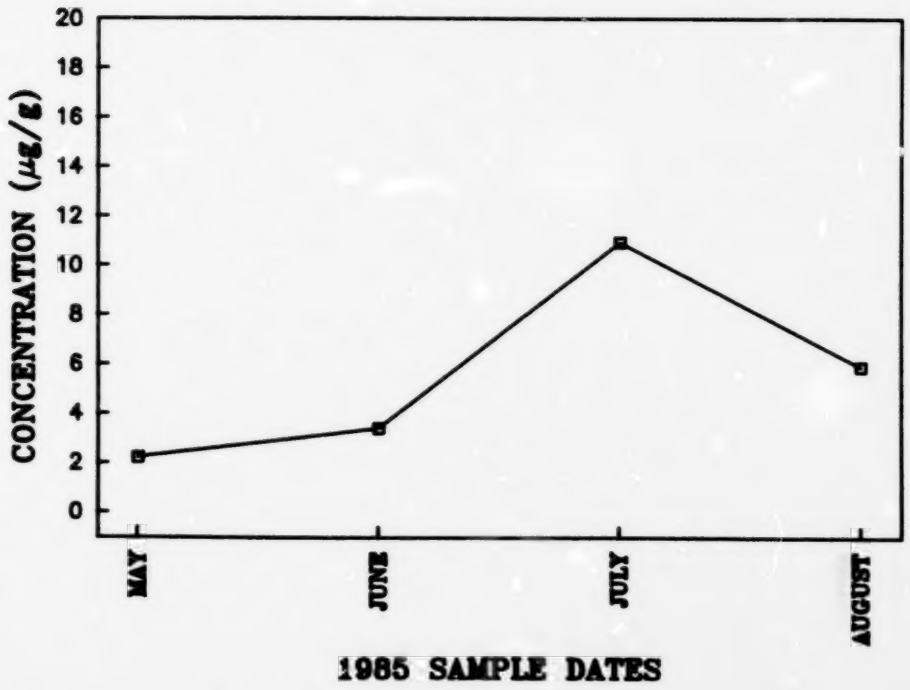


FIGURE 6.2.3.1.8 CONCENTRATION OF CHRYSENE IN SITE C TOPSOIL

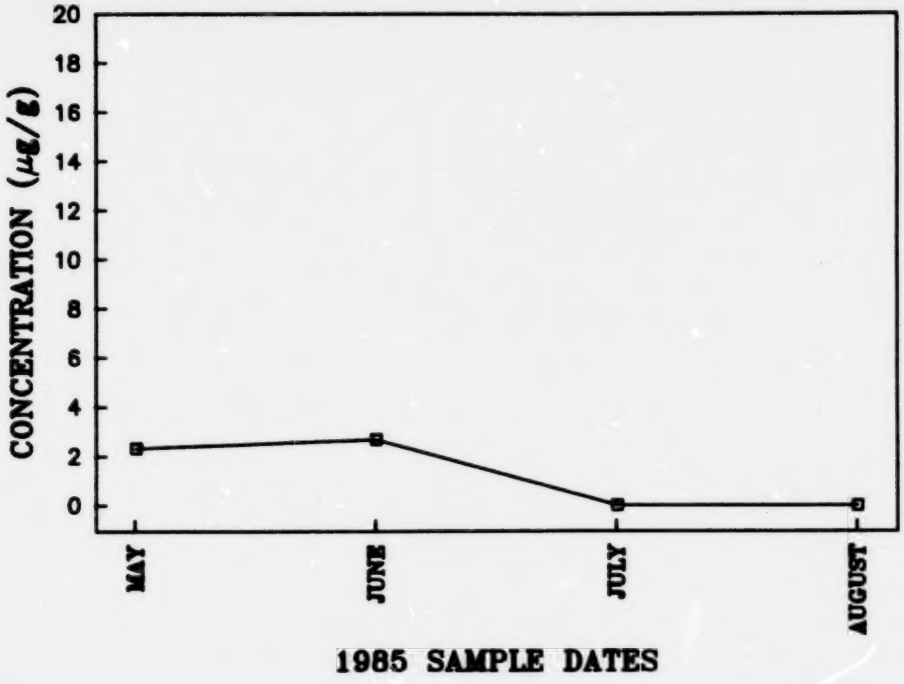


FIGURE 6.2.3.1.9 CONCENTRATION OF BENZO(A)ANTHRACENE IN SITE C TOPSOIL

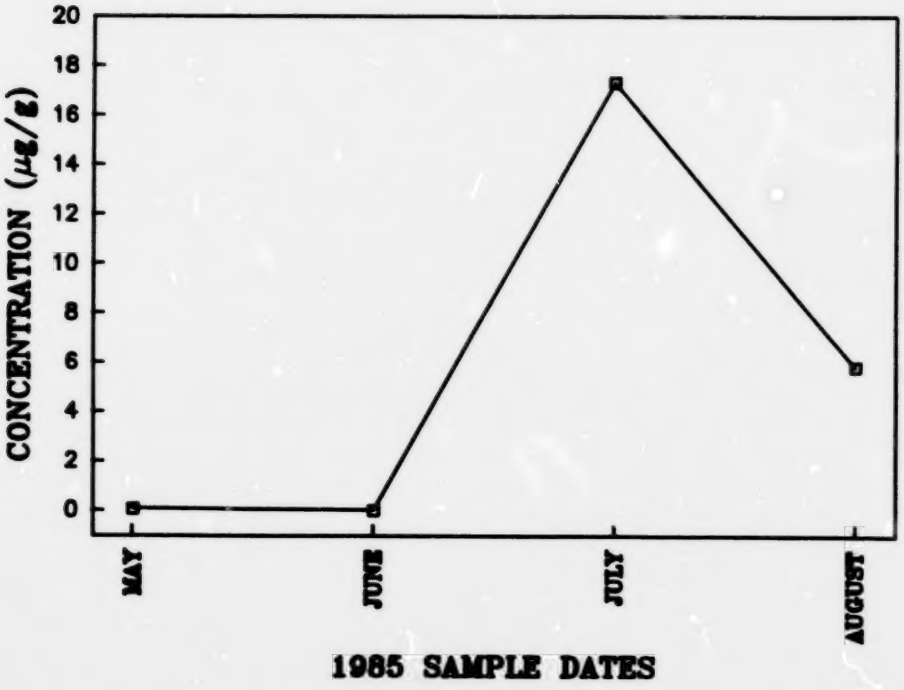


FIGURE 6.2.3.1.10 CONCENTRATION OF BENZO(B/K)FLUORANTHENE IN SITE C TOPSOIL

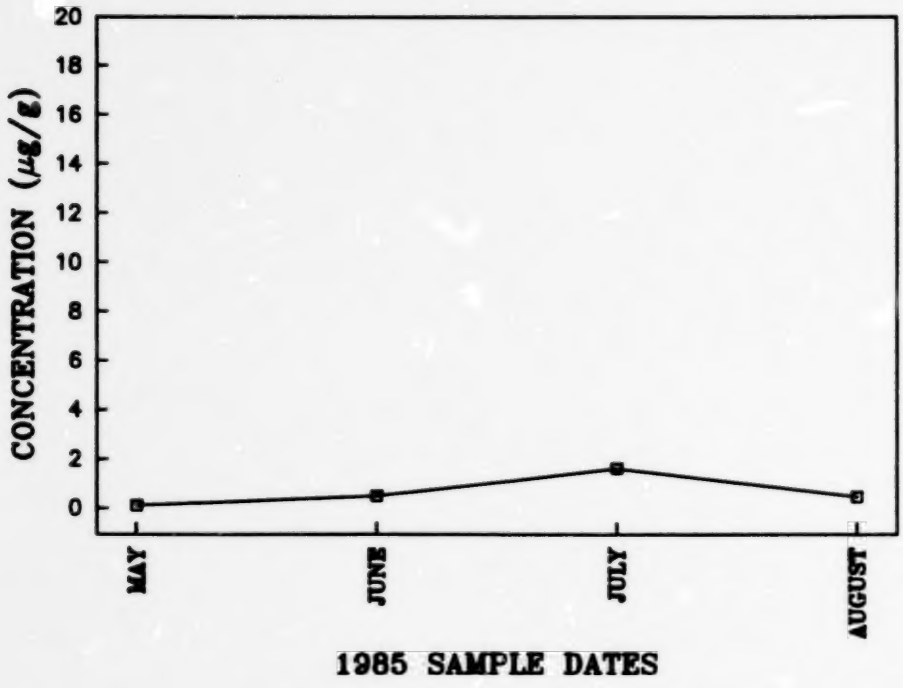


FIGURE 6.2.3.1.11 CONCENTRATION OF BENZO(A)PYRENE IN SITE C TOPSOIL

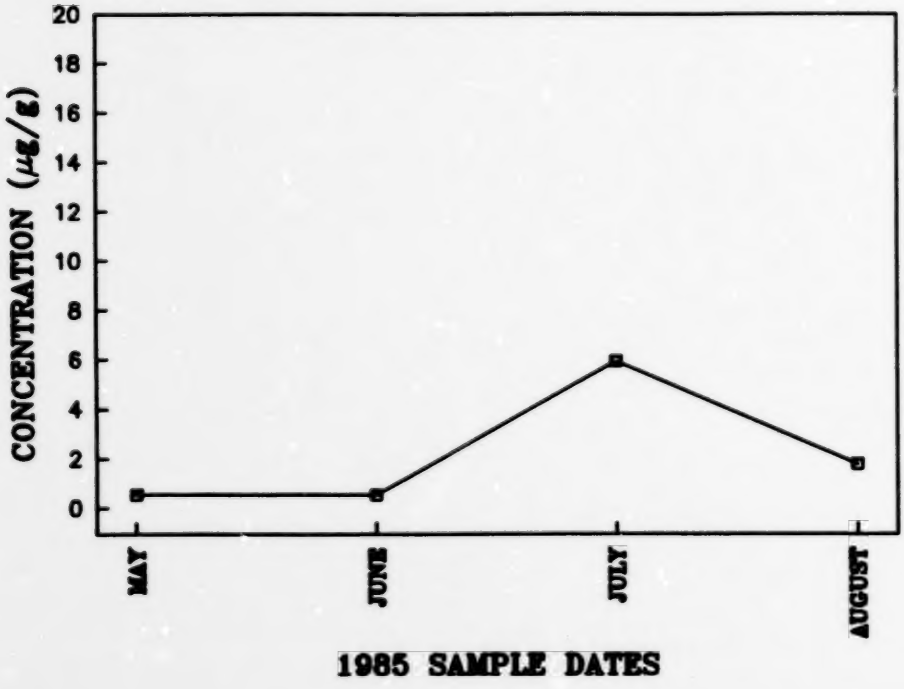


FIGURE 6.2.3.1.12 CONCENTRATION OF DIBENZO(A,H)ANTHRACENE IN SITE C TOPSOIL

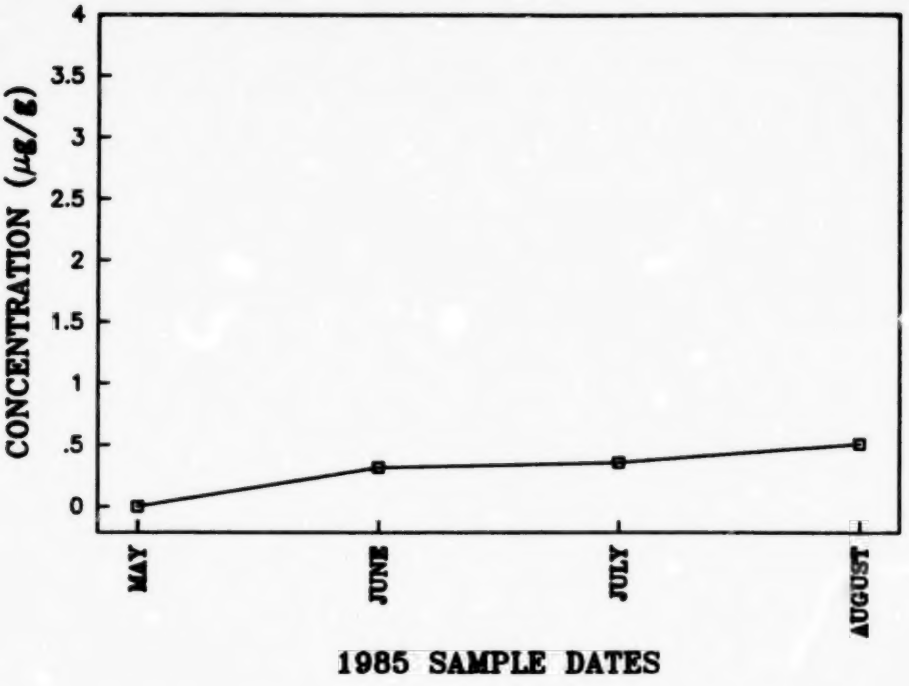


FIGURE 6.2.3.1.13 CONCENTRATION OF BENZO(G,H,I)PERYLENE IN SITE C TOPSOIL

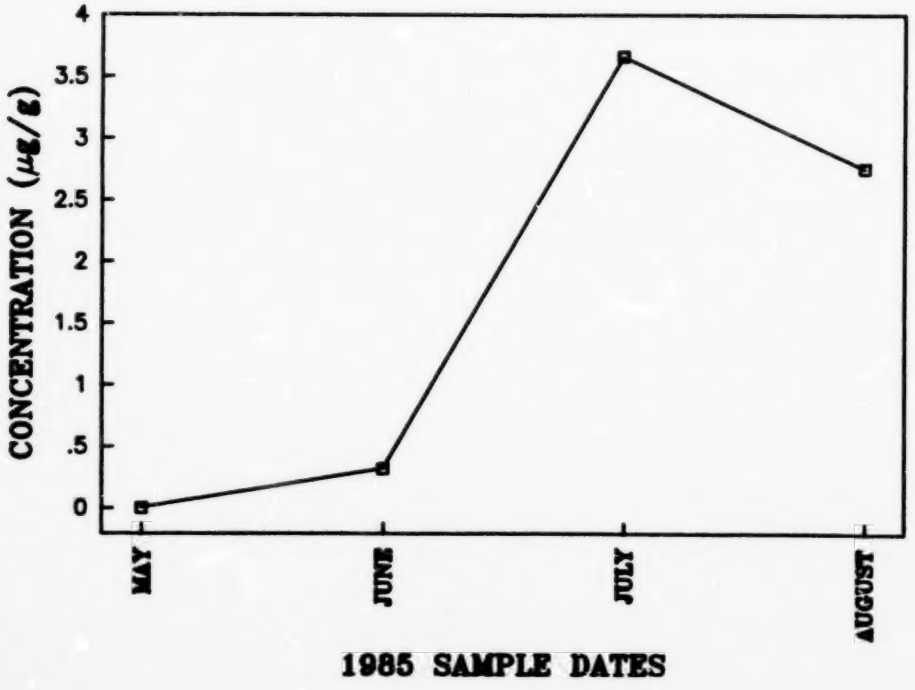


FIGURE 6.2.3.1.14 OIL IN SITE C TOPSOIL

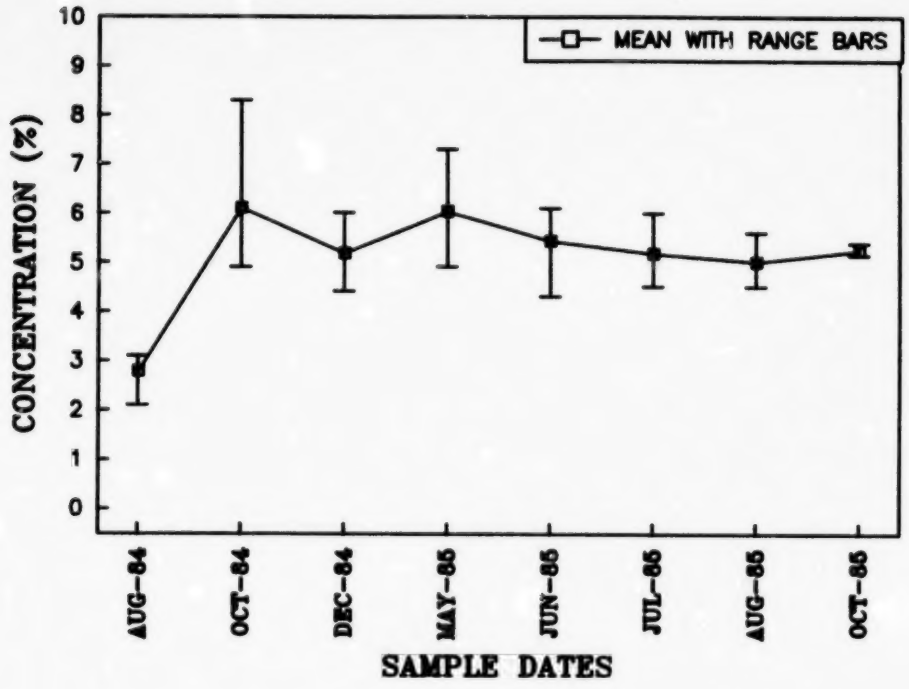


FIGURE 6.2.3.1.15 OIL VERSUS METALS CONTENT IN SITE C SOIL

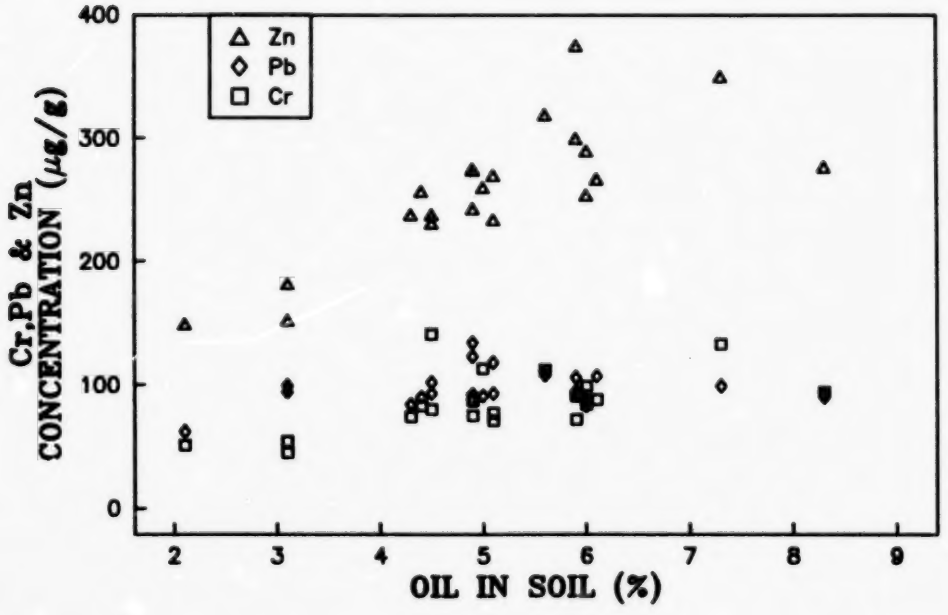


FIGURE 6.2.3.2.1 DOC IN WELLWATER (mg/L) SITE C - MAY 1985

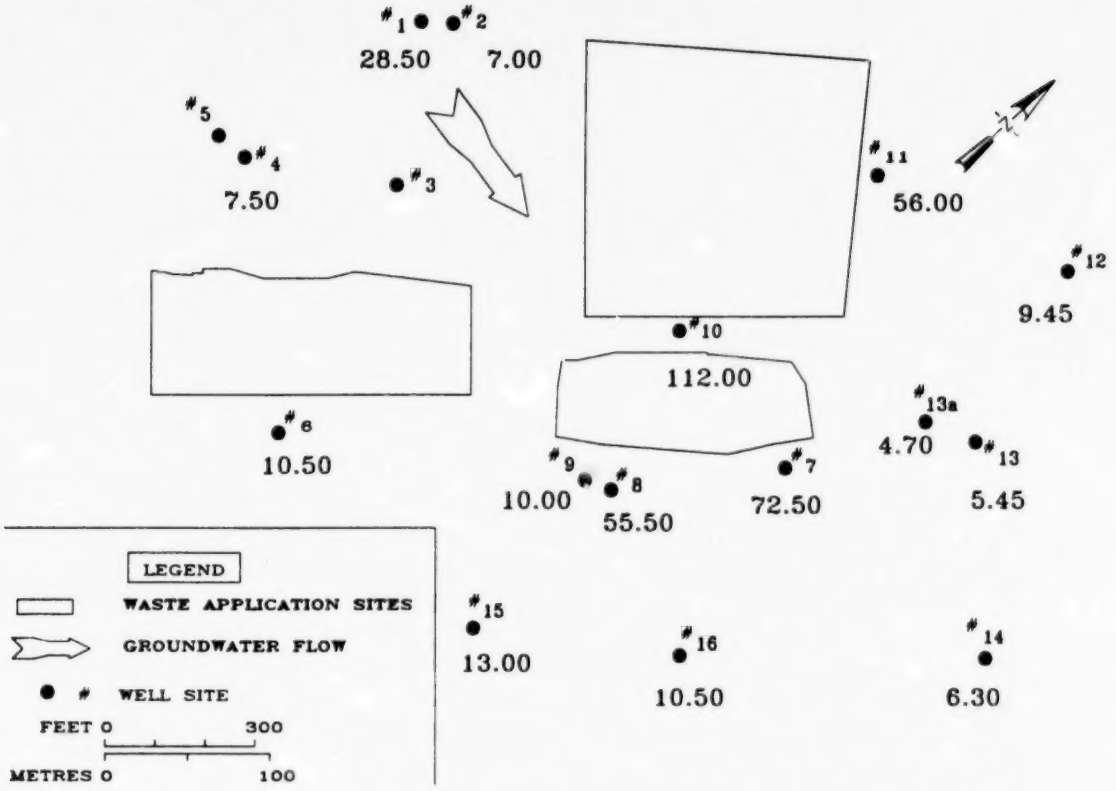


FIGURE 6.2.3.2.2 TOTAL PAH IN WELLWATER (µg/L) SITE C - MAY 1985

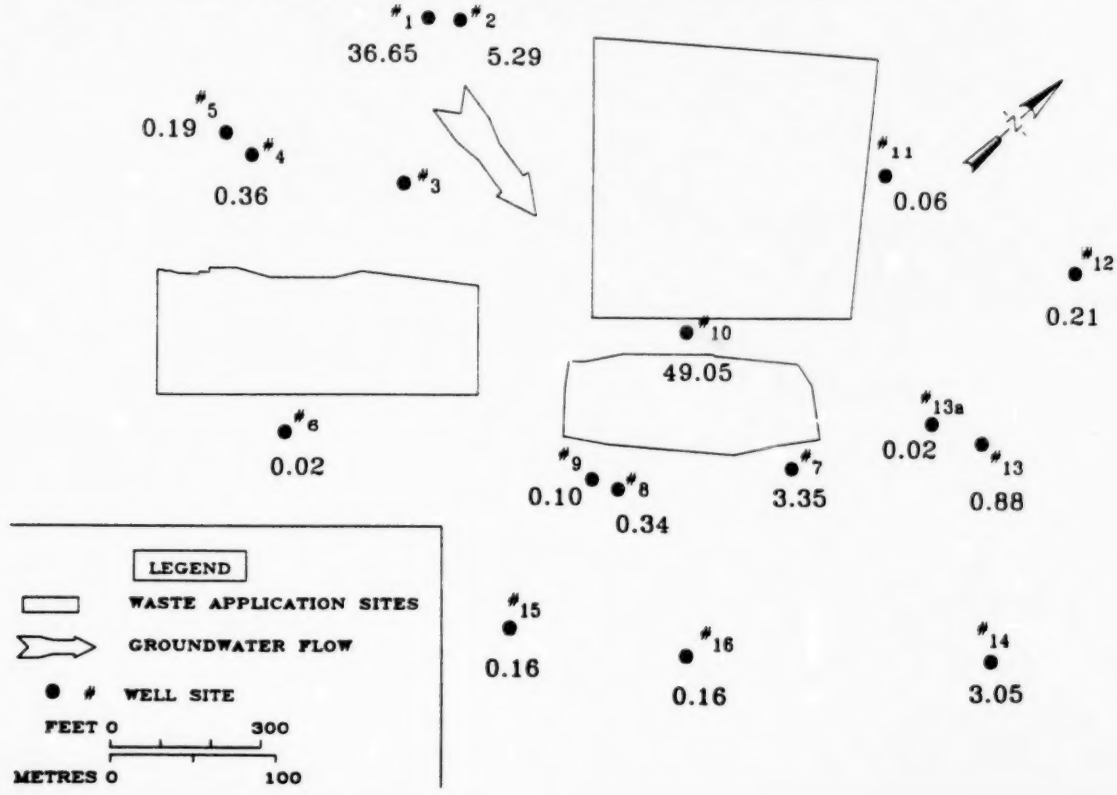


FIGURE 6.2.3.2.3 DOC IN WELLWATER (mg/L) SITE C - AUGUST 1985

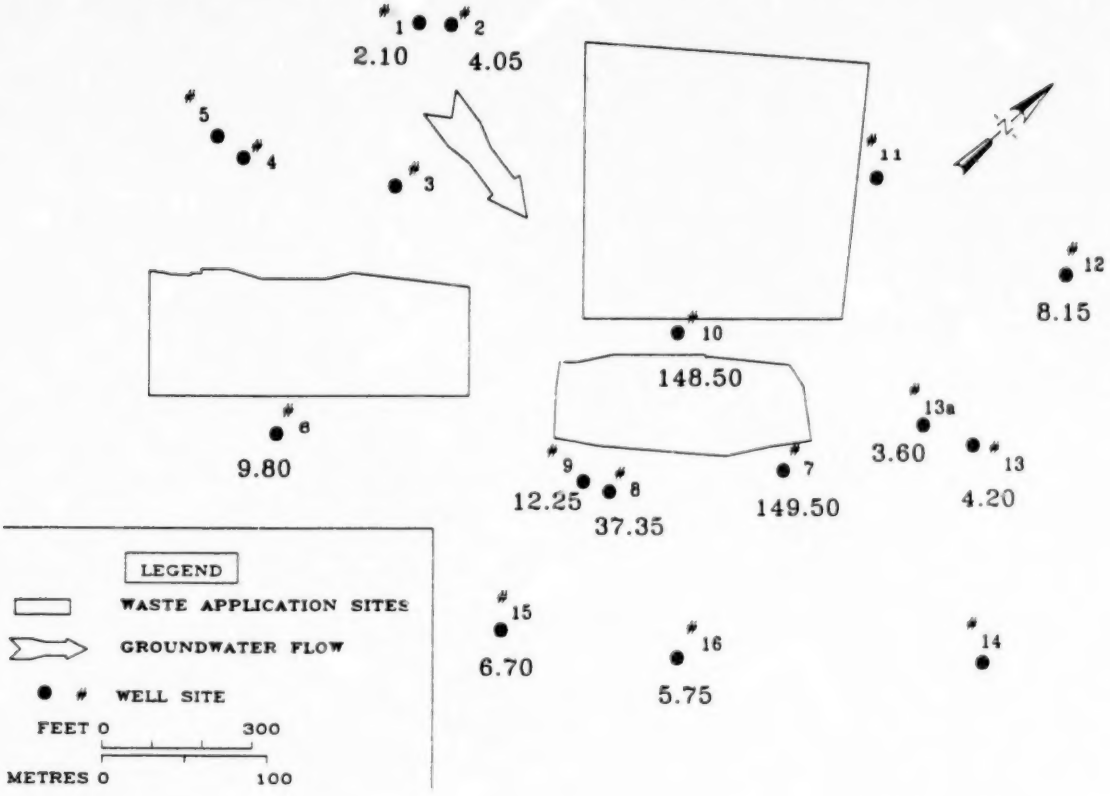


FIGURE 6.2.3.2.4 TOTAL PAH IN WELLWATER (µg/L) SITE C - AUGUST 1985

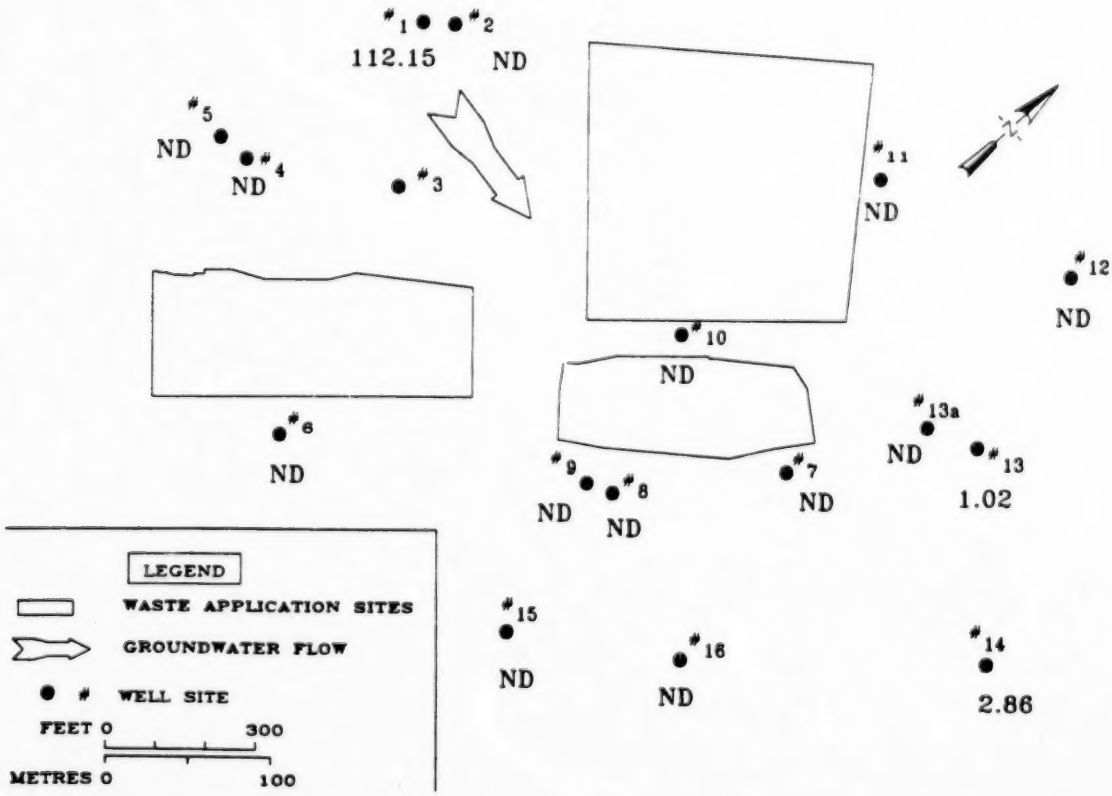


FIGURE 6.2.3.2.5 DOC IN SITE C WELLWATER - BACKGROUND WELLS

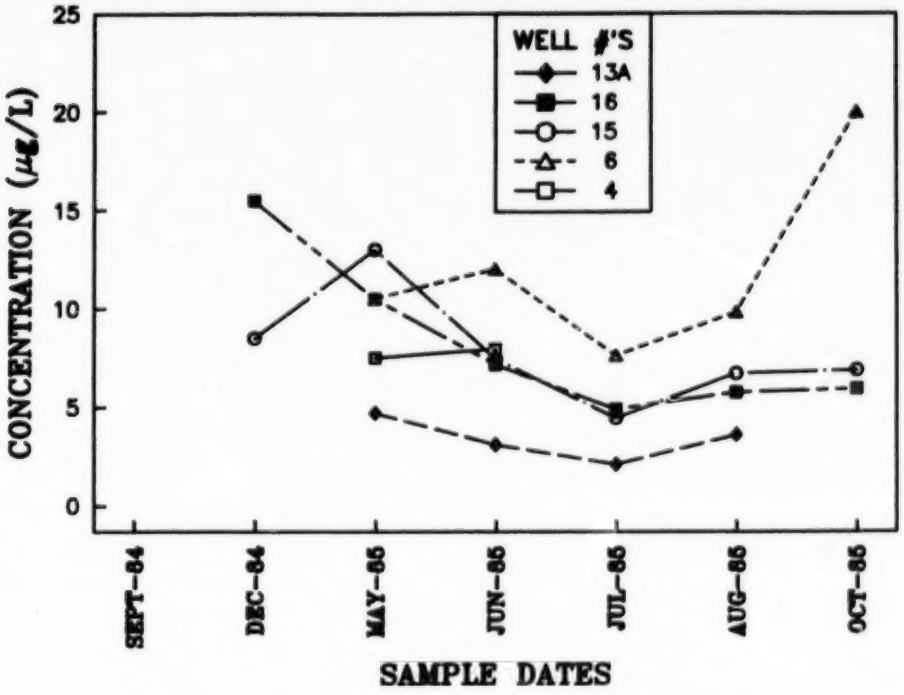


FIGURE 6.2.3.2.6 TOTAL PAH IN SITE C WELLWATER - BACKGROUND WELLS

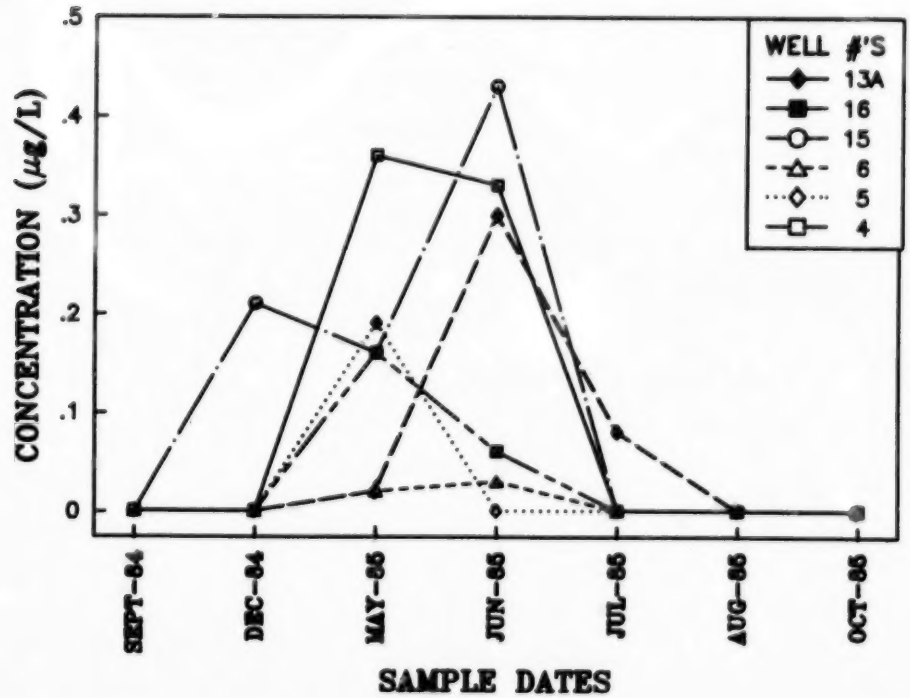


FIGURE 6.2.3.2.7 PROPORTIONS OF PAH'S IN SITE C WELLWATER GROUPED BY MOLECULAR WEIGHT - WELL #15

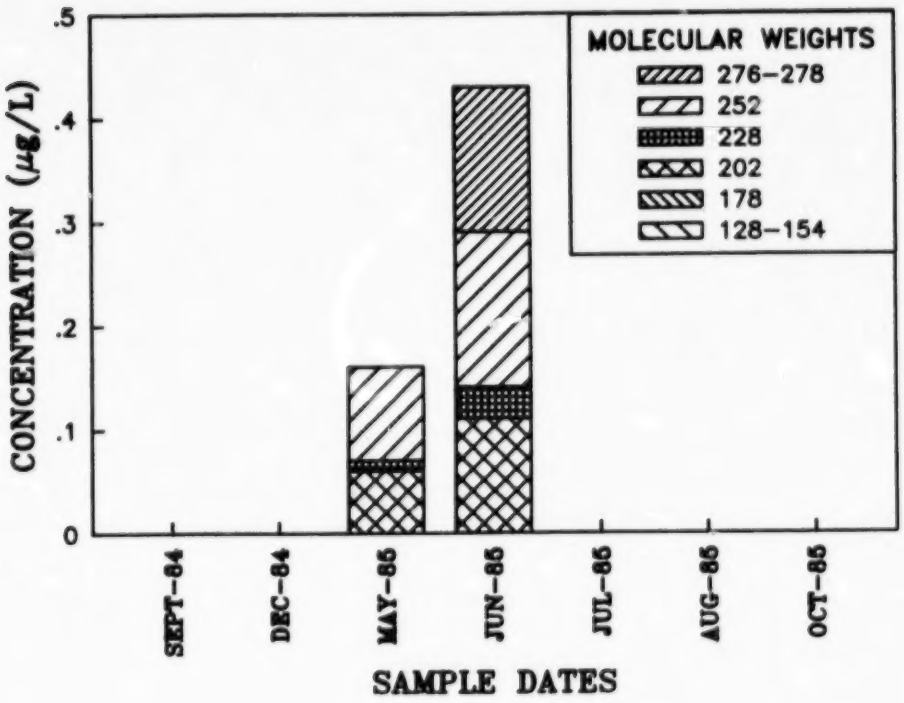


FIGURE 6.2.3.2.8 DOC IN SITE C WELLWATER - WELLS NEAR LANDFARM AREA

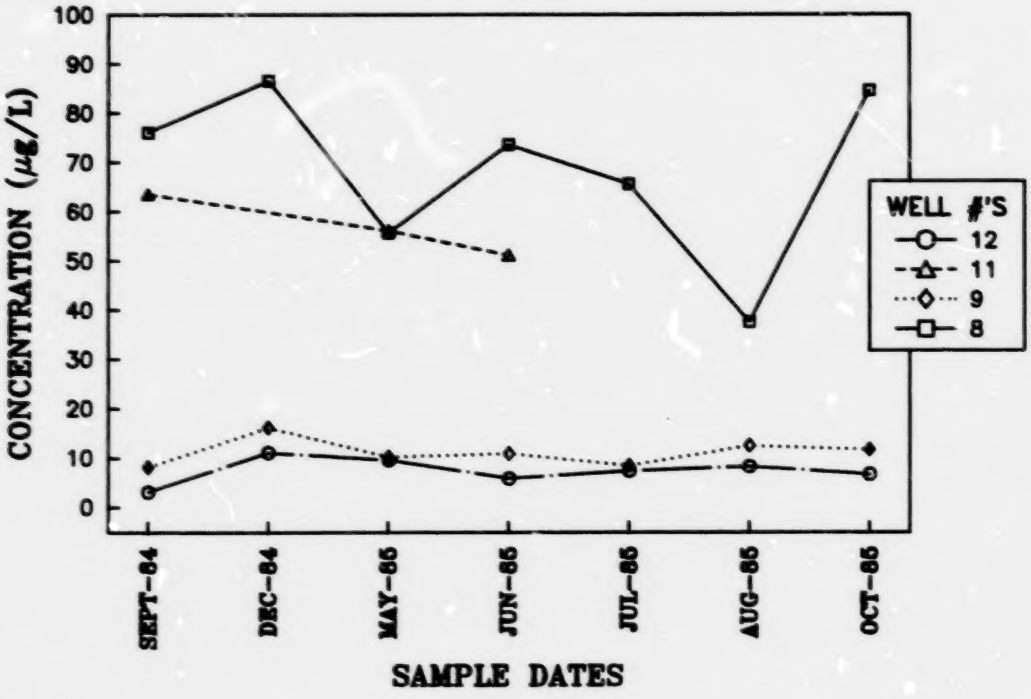


FIGURE 6.2.3.2.9 TOTAL PAH IN SITE C WELLWATER - WELLS NEAR LANDFARM AREA

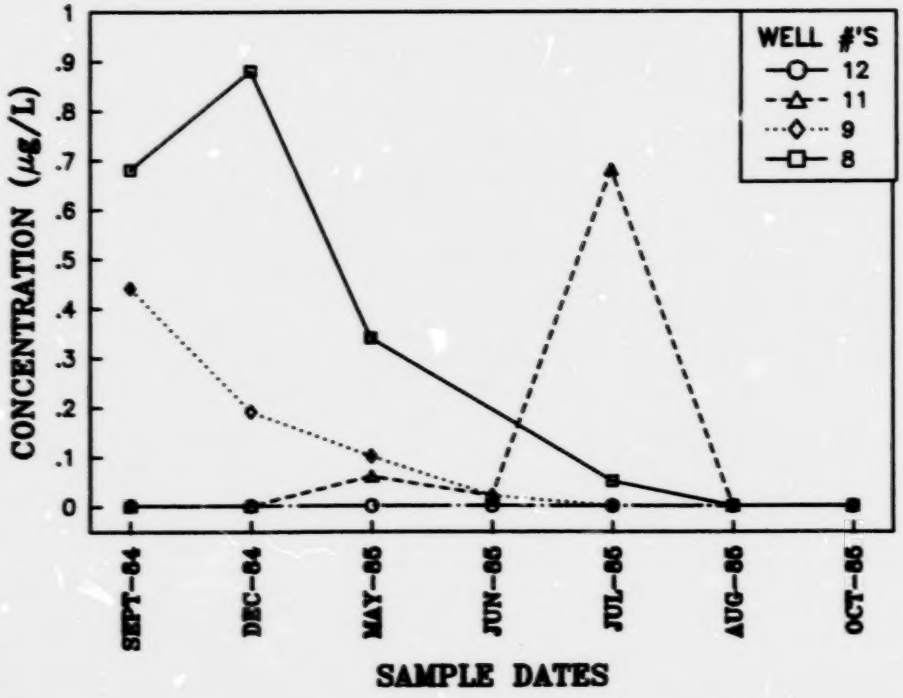


FIGURE 6.2.3.2.10 PROPORTIONS OF PAH'S IN SITE C WELLWATER GROUPED BY MOLECULAR WEIGHT - WELL #12

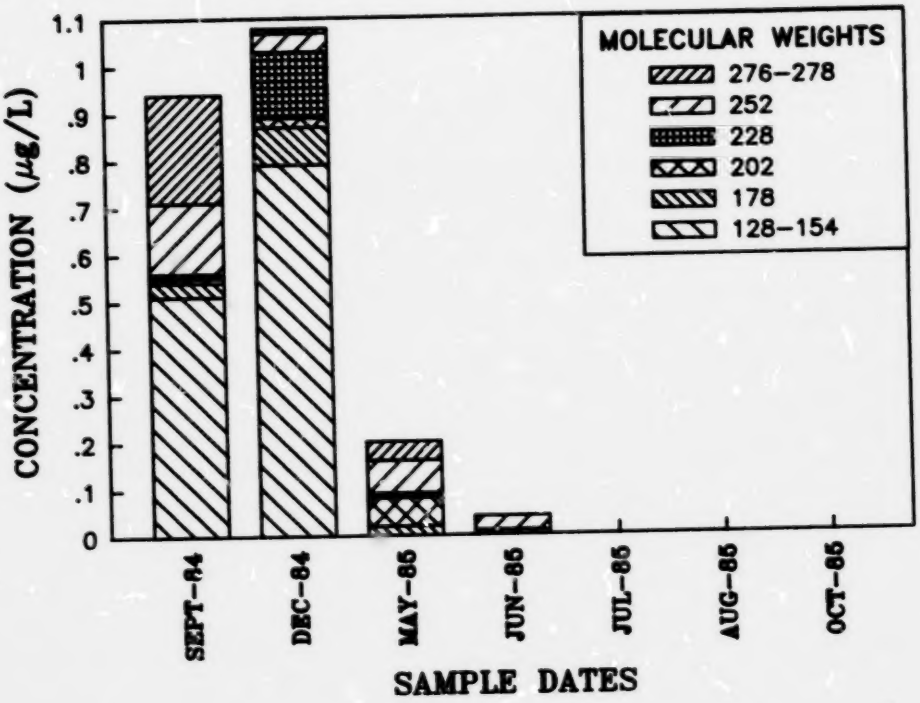


FIGURE 6.2.3.2.11 CONCENTRATION OF CHRYSENE IN SITE C WELLWATER - WELLS NEAR LANDFARM

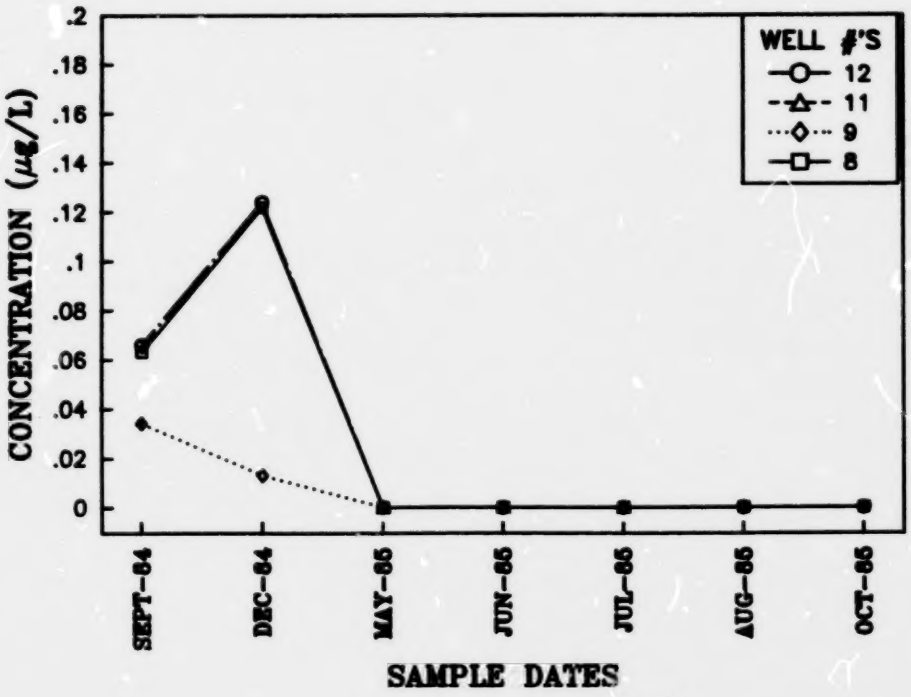


FIGURE 6.2.3.2.12 CONCENTRATION OF DIBENZO(A,H)ANTHRACENE IN SITE C WELLWATER - WELLS NEAR LANDFARM

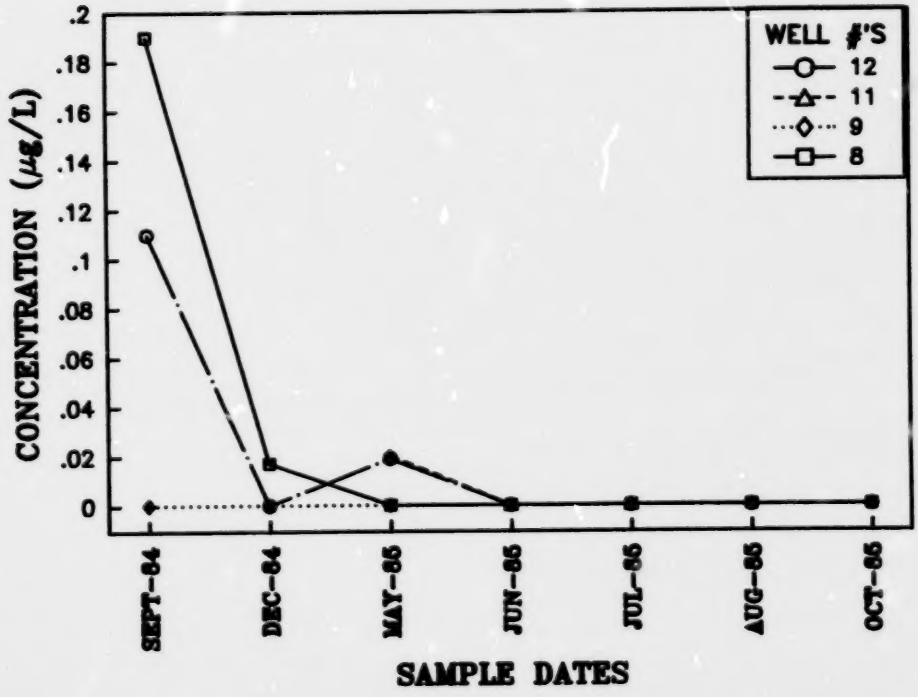


FIGURE 6.2.3.22.13 CONCENTRATION OF BENZO(A)PYRENE IN SITE C WELLWATER WELLS - NEAR LANDFARM

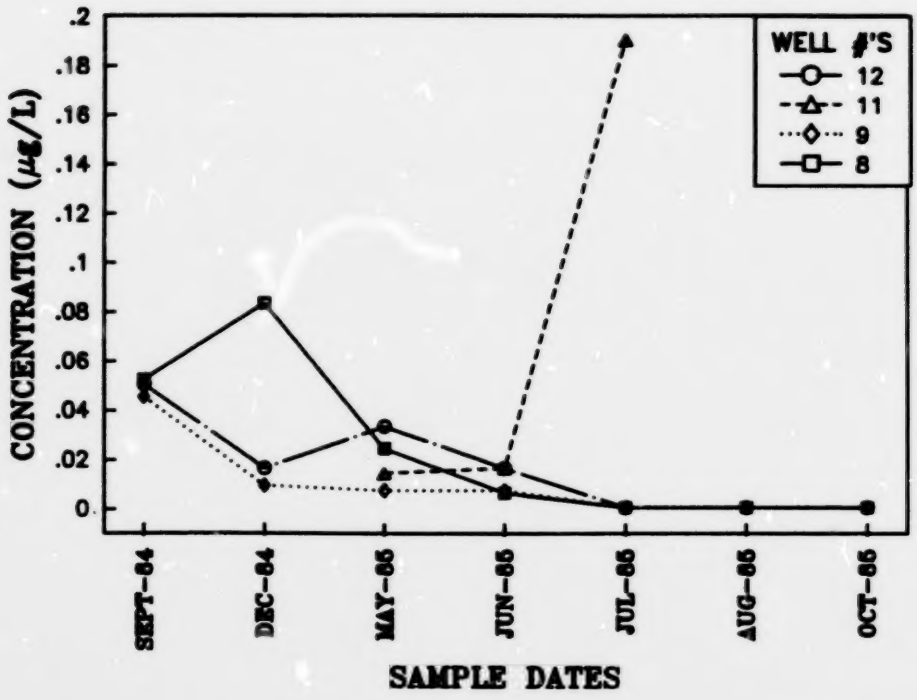


FIGURE 6.2.3.2.14 CONCENTRATION OF BENZO(G,H,I)PERYLENE IN SITE C WELLWATER - WELLS NEAR LANDFARM

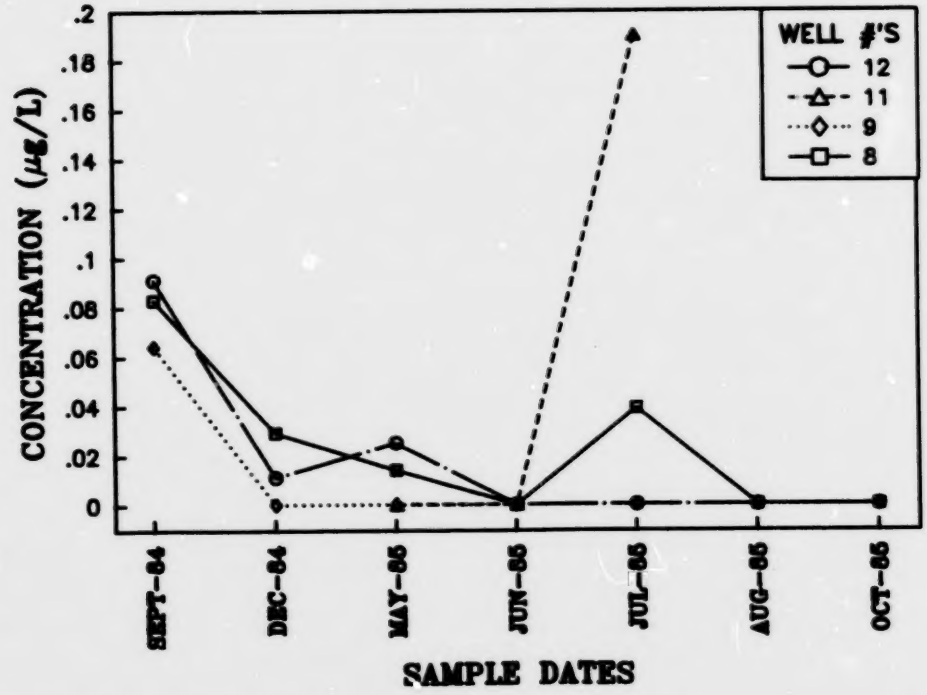


FIGURE 6.2.3.2.15 DOC IN SITE C WELLWATER - WELLS NEAR SEWAGE LINE

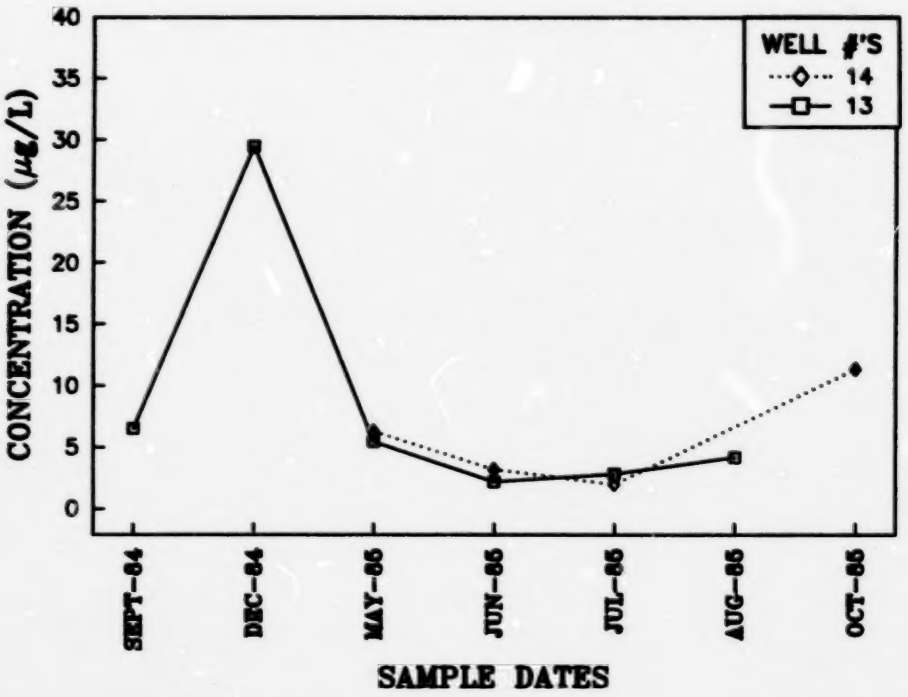


FIGURE 6.2.3.2.16 TOTAL PAH IN SITE C WELLWATER - WELLS NEAR SEWAGE LINE

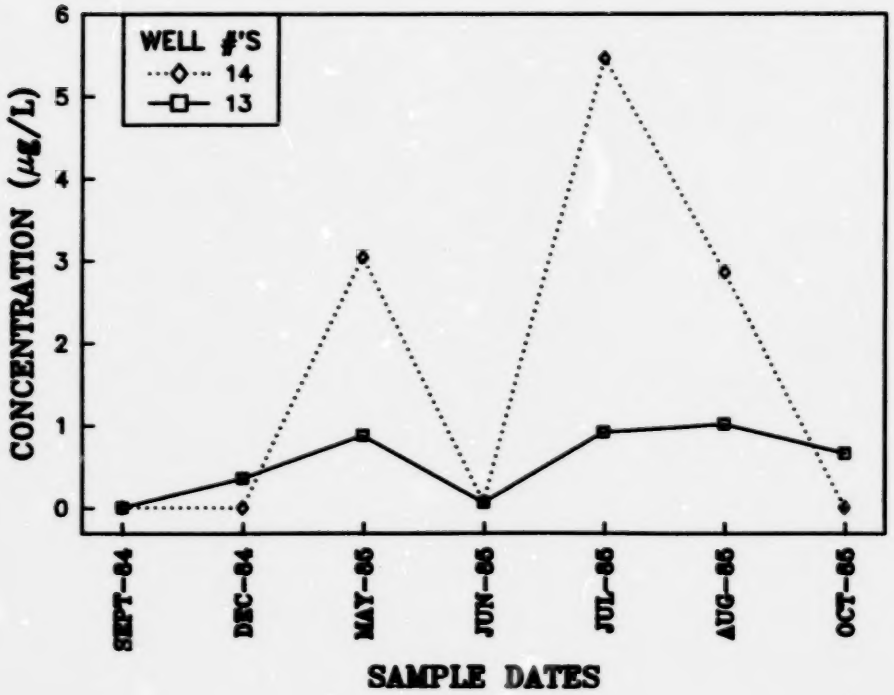


FIGURE 6.2.3.2.17 PROPORTIONS OF PAH'S IN SITE C WELLWATER
GROUPED BY MOLECULAR WEIGHT - WELL #13

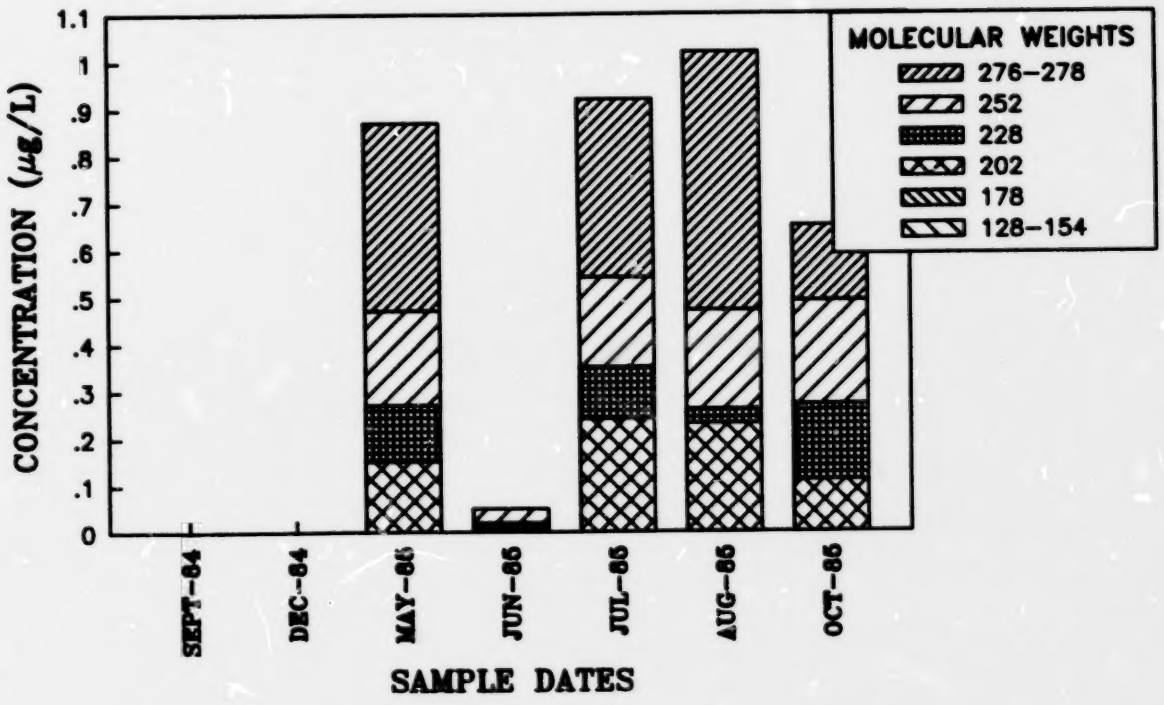


FIGURE 6.2.3.2.18 CONCENTRATION OF CHRYSENE IN SITE C WELLWATER - WELLS NEAR SEWAGE LINE

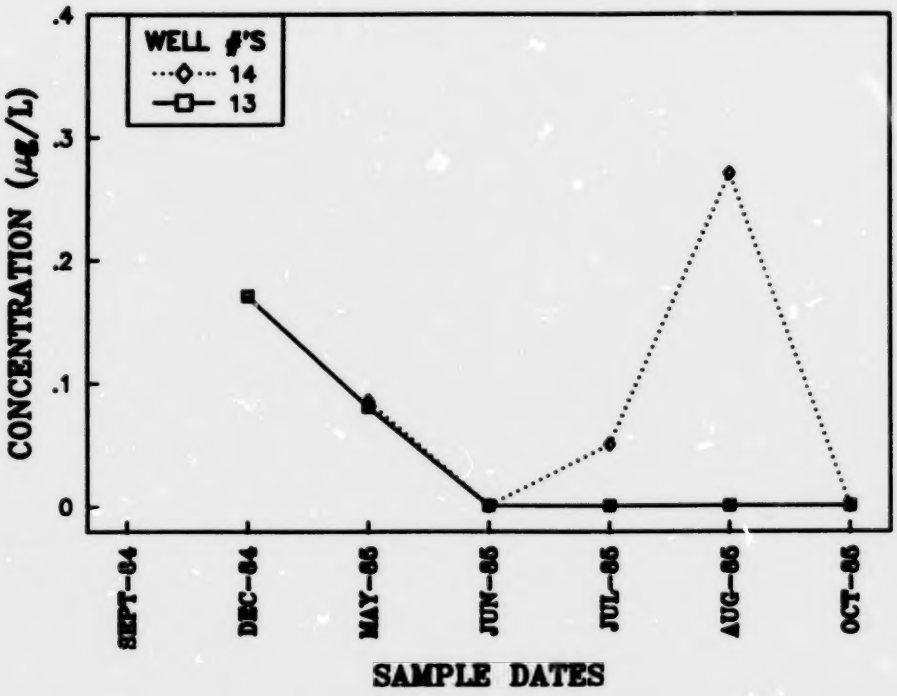


FIGURE 6.2.3.2.19 CONCENTRATION OF DIBENZO(A,H)ANTHRACENE IN SITE C WELLWATER - WELLS NEAR SEWAGE LINE

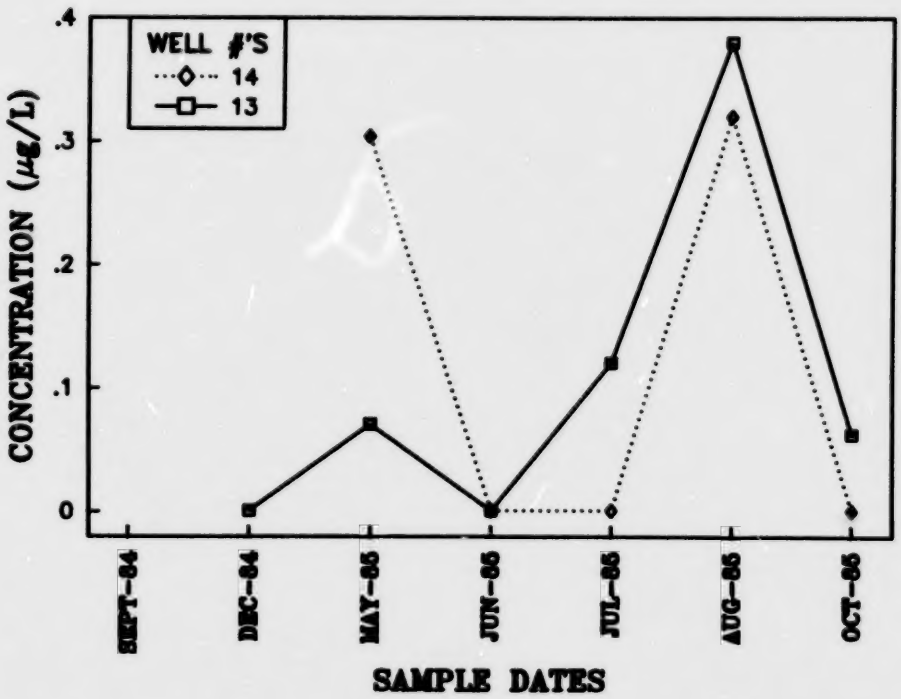


FIGURE 6.2.3.2.20 CONCENTRATION OF BENZO(A)PYRENE IN SITE C WELLWATER - WELLS NEAR SEWAGE LINE

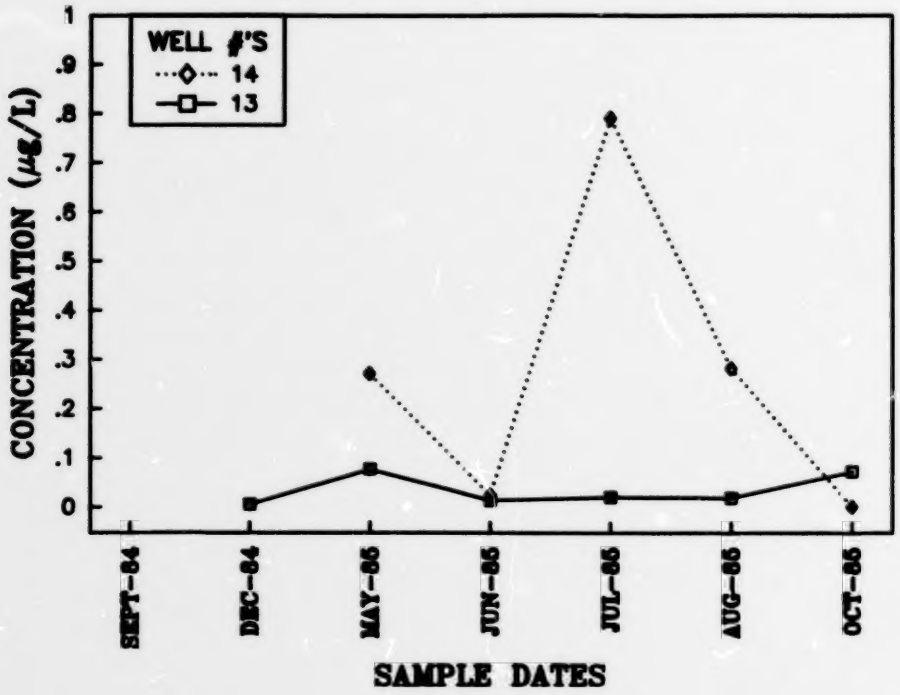


FIGURE 6.2.3.2.21 CONCENTRATION OF BENZO(G,H,I)PERYLENE IN SITE C WELLWATER - WELLS NEAR SEWAGE LINE

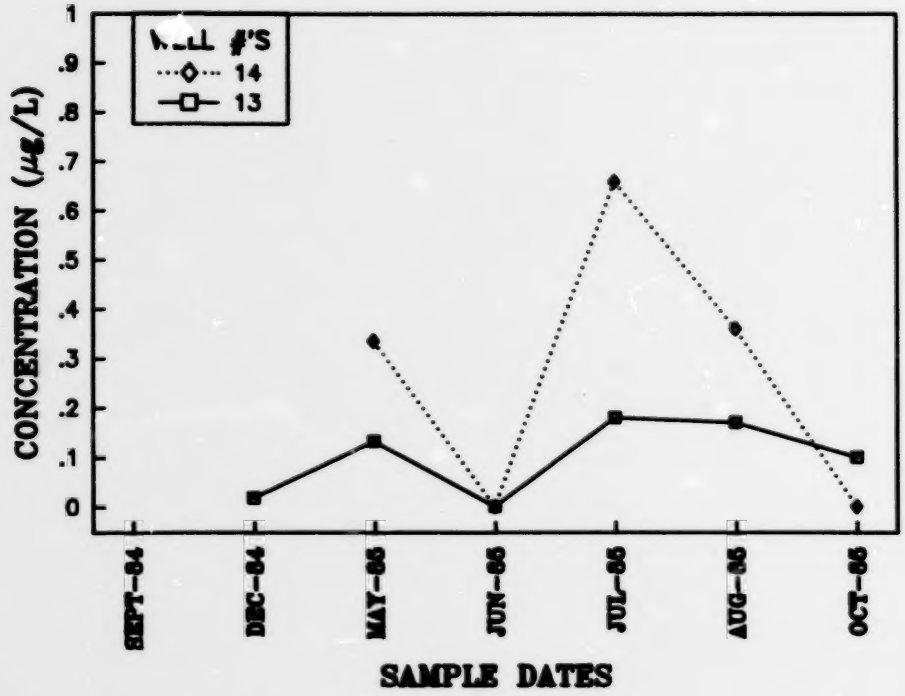


FIGURE 6.2.3.2.22 DOC IN SITE C WELLWATER - CONTAMINATED WELLS

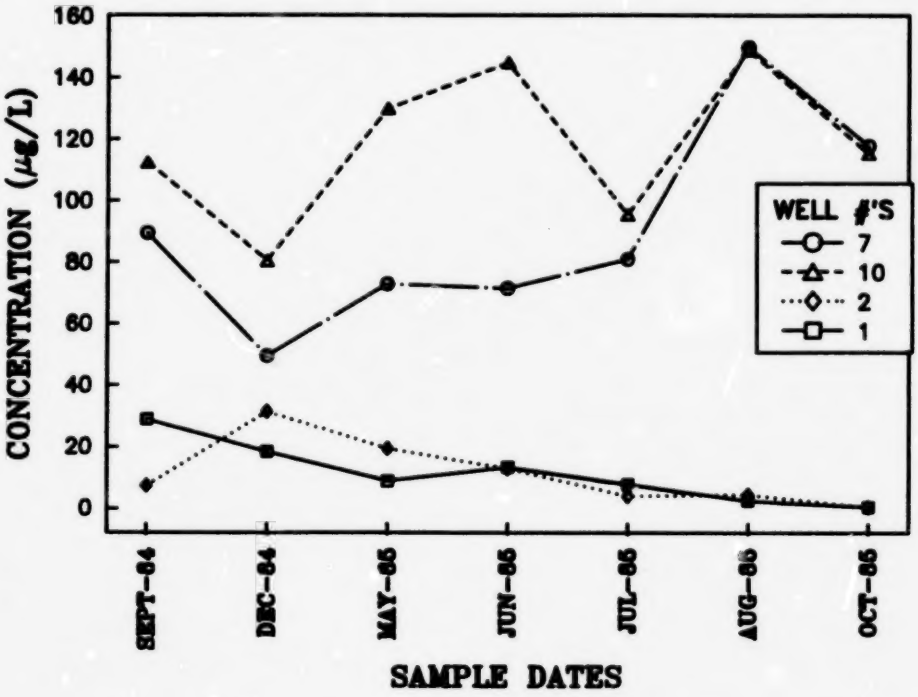


FIGURE 6.2.3.2.23 TOTAL PAH IN SITE C WELLWATER - CONTAMINATED WELLS

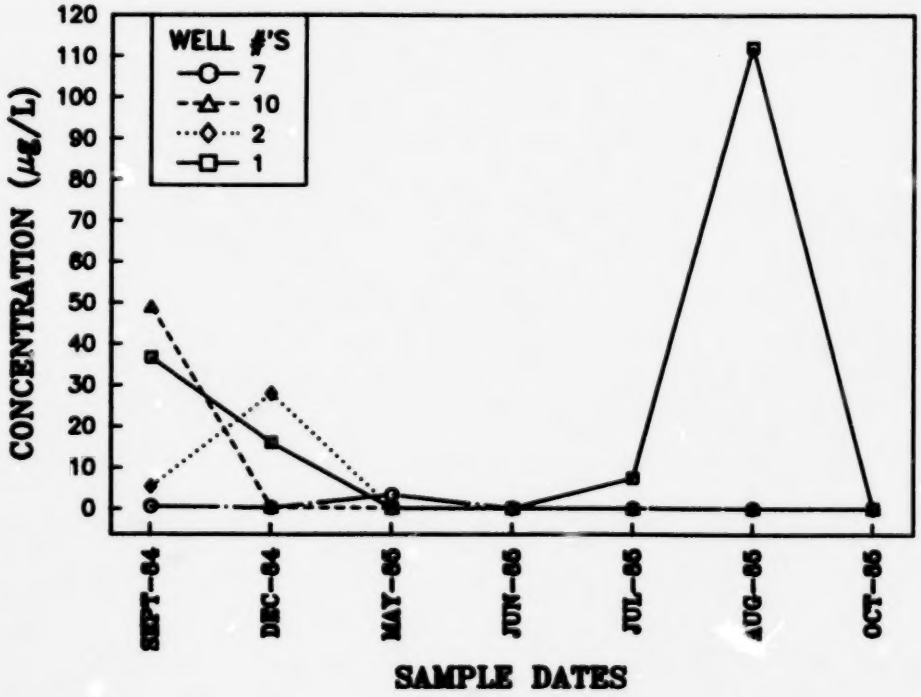


FIGURE 6.2.3.2.24 PROPORTIONS OF PAH'S IN SITE C WELLWATER GROUPED BY MOLECULAR WEIGHT - WELL #1

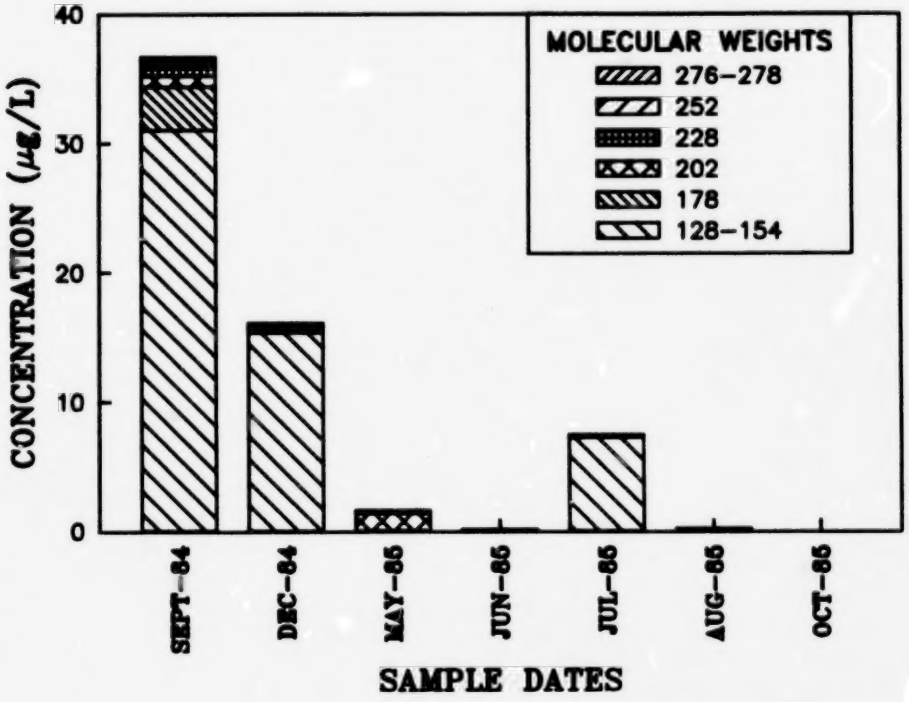
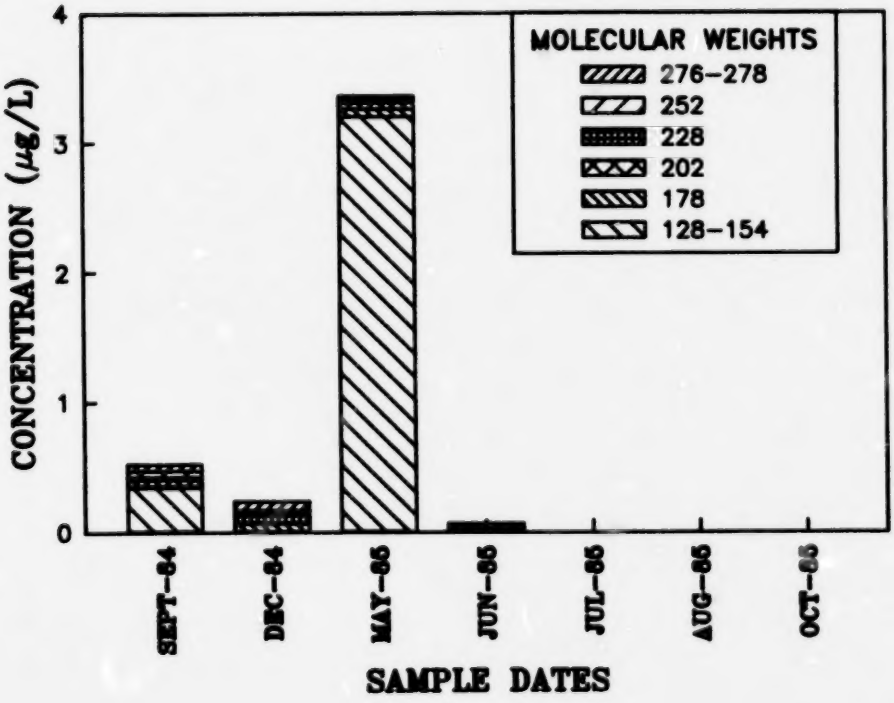


FIGURE 6.2.3.2.25 PROPORTIONS OF PAH'S IN SITE C WELLWATER GROUPED BY MOLECULAR WEIGHT - WELL #7



6.2.4 Discussion of Landfarm Results

Landfarm soil sampling was intended to provide estimates of PAH persistence in soil in a field situation, for comparison with laboratory data. Soil sampling in the laboratory assesses loss of PAH from soil resulting only from degradation and volatilization. Loss from soil in a field situation could also occur by transport of PAH through soil and into groundwater. Sampling of groundwater at the sites was therefore performed to determine if movement of PAH out of the surface soil was a substantial pathway of PAH loss contributing to environmental contamination.

The results of this monitoring program suffered from the same analytical difficulties as described in Section 6.1.2 for the kinetic study. The extent to which the objectives could be met was therefore limited. The study provided an opportunity, however, to compare the efficiency of oily waste treatment at three locations with different site and operational conditions.

For comparison of field and laboratory data, the most direct comparison can be made between the laboratory results and results from site C, as the same soil was used. Overall oil and grease loss from site C soil was similar in the laboratory and field, with a loss from 6% to 5% oil (17% reduction from initial oil and grease content) over the 120 day summer season (May to September) in the field and a similar loss over 120 days in the laboratory. Greater precision was obtained with laboratory results and some kinetic parameters were estimated. Losses from sites A and B over the same 120 day field season were from 0.3% to 0.2% oil and 2.3% to 1.5% oil (approximately 33% and 35% of initial oil and grease), respectively.

Concentration of both oil and PAH varied for the three sites and may have been related to previous landfarm activities. Exactly which activities contributed to higher PAH levels in soil could not be identified, however, as little detail was available on the history of application at sites B and C. Site A had received waste applications of less than 1% oil for a three year period, whereas sites B and C had a history of 10 years or more of waste application at levels greater than 1% oil and concentrations of PAH were significantly greater than background.

Concentrations of PAH at site A were too low to assess loss over time. Data from sites B and C were compared with laboratory data, however. Chrysene was the only PAH that appeared to decrease over 90 to 120 days in the field. This observation was not confirmed by the laboratory study, in which no decrease of chrysene was observed over a 250 day period. No loss of pyrene, benzo(b/k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene or benzo(g,h,i)perylene was observed in either the field or laboratory within a 120 day period, although pyrene did decrease in laboratory soil after 200 days.

In some instances, the concentrations of these PAH's appeared to increase in the field soil over the monitoring period. This observation was not confirmed by laboratory results, however. Considering the variability in recovery for these samples, it is likely that the observed increases are due to analytical variability and interferences. The results do suggest that there is the potential for these high molecular weight PAH to accumulate in soil with site B and C operating conditions. The highest PAH

concentrations were observed at site C, which also had the highest oil content. Total PAH (summation of 16 PAH concentrations) increased over the field season at both sites B and C, although oil content appeared to increase only at site C. Oil content in soil appeared to give a relative estimate of the PAH content of the soil, but was not useful in estimating loss of PAH over a specific field season.

Concentrations of PAH's in groundwater were found to be elevated over background concentrations on sites B and C, which also had substantially elevated PAH concentrations in soil. Although the movement of PAH through soil or groundwater was not studied in detail, the proximity of high concentrations of PAH's to landfarm areas suggested that the waste application sites were, in fact, a source of PAH's. The relative concentration of PAH in groundwater at the three sites also appeared to correspond to the relative PAH content in the landfarm soil, i.e. was greatest at site C and as low as background concentrations at site A. Other potential sources for PAH contamination on sites B and C were also identified, however. In fact, the highest concentrations of PAH observed in groundwater, other than those due to direct contamination with fuel, were those associated with a sewage trunk line on site C. Although transport of PAH's from landfarm soil did appear to be one mechanism for loss from soil on sites B and C, the environmental significance of transport from landfarm soil has not been assessed.

6.3 Part 3 - Incubations with ^{14}C-labelled PAH

The Part 3 study involved a detailed assessment of the fate of naphthalene, anthracene and benzo(a)pyrene in soil using a laboratory incubation procedure with ^{14}C-labelled chemicals. In addition, the effects of nutrient addition, soil pH and sterilization were studied. The results provided a mass balance of ^{14}C in soil and air for each of the target chemicals. With each chemical studied, the ^{14}C label was not placed uniformly over the entire molecule. Thus the tracing of ^{14}C within the soil system did not follow all portions of the molecule, but indicated whether the parent molecule persisted or was converted into some form of transformation product.

6.3.1 Microbial activity in biometer flask incubations

Total CO_2 evolution was measured throughout the experiments to confirm that the treatments or environmental conditions did not result in unforeseen or undesirable effects on microbial activity in the flasks. For example, it was necessary to determine that sterilization with $HgCl_2$ was effective throughout the incubation period, and that biological activity was maintained in the treatments which were not sterilized. For a comparison of the results obtained with the different PAH additions, it was also desirable to be able to compare overall microbial activity for each study.

Figures 6.3.1.1-3a illustrate the rates of total CO_2 evolution from biologically active soils with ^{14}C-benzo(a)pyrene, ^{14}C-naphthalene and ^{14}C-anthracene addition, respectively. In previous studies using biometer flasks, the moisture content of the soil remained very stable over a 6 month period. In the benzo(a)pyrene study, however, a decline in total CO_2 evolution from unsterilized soil to the level observed in sterilized flasks after 60 days indicated that the soil had dried substantially (this oily soil is not visibly different whether wet or dry). Regular moisture additions were made following day 60. The problem was obviated in the naphthalene and anthracene studies by monitoring moisture content gravimetrically and making weekly water additions. Figure 6.3.1.3b illustrates the rate of total CO_2 evolved from sterilized soil with anthracene addition. The low level of CO_2 evolution, zero for most sample periods, was similar to that observed for studies with benzo(a)pyrene and naphthalene.

Reduction of soil pH to 4.5 resulted in somewhat reduced metabolic activity in the benzo(a)pyrene study. This effect did not last throughout the incubation period, however, as the pH gradually increased due to the buffering capacity of the soil and was measured as 6.5 - 7.0 at the end of the 6 month incubation. It was concluded that the low pH treatment was not effective in the benzo(a)pyrene study. In the studies with naphthalene and anthracene, this problem was minimized by making periodic additions of acidified water to the pH 4.5 treatments. Maintaining the low pH did not substantially reduce overall metabolic activity during the course of these studies.

The addition of $HgCl_2$ effectively sterilized the soil for the entire incubation period in most cases. In the anthracene study, however, sterilization appeared to be incomplete with the pH 4.5 treatment. For

FIGURE 6.3.1.1 BENZO(A)PYRENE - RATE OF TOTAL CO_2 EVOLVED BIOLOGICALLY ACTIVE SOIL

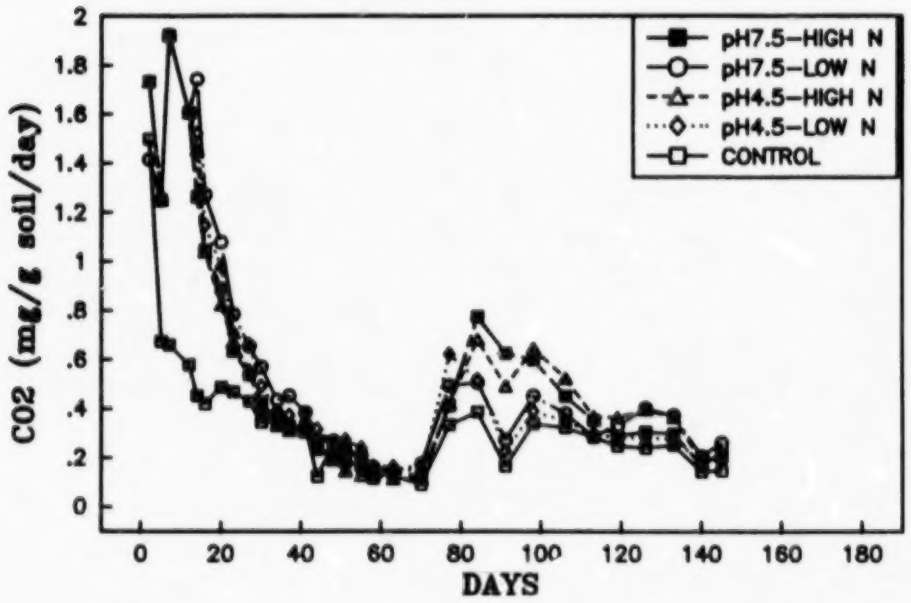


FIGURE 6.3.1.2 NAPHTHALENE - RATE OF TOTAL CO_2 EVOLVED BIOLOGICALLY ACTIVE SOIL

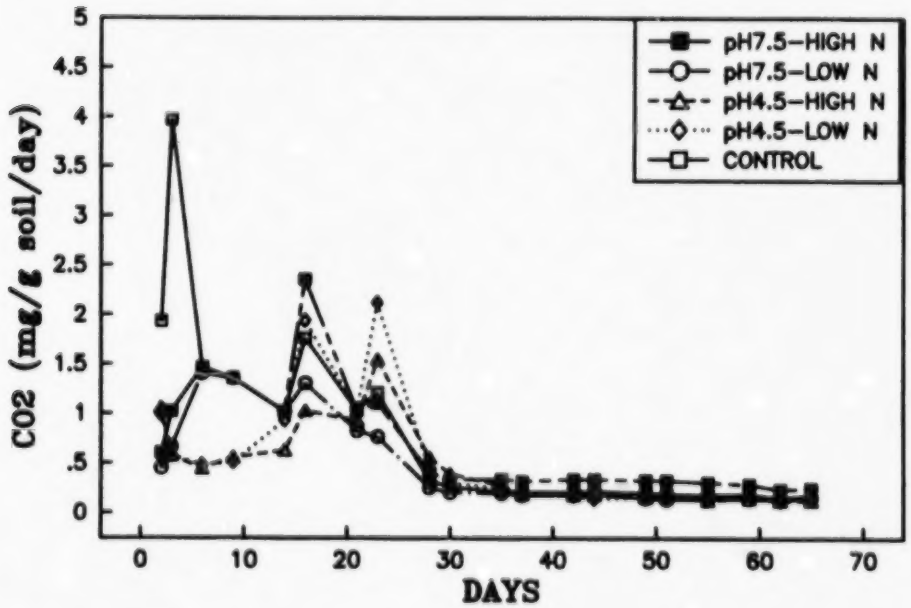


FIGURE 6.3.1.3 ANTHRACENE - RATE OF TOTAL CO_2 EVOLVED
BIOLOGICALLY ACTIVE SOIL

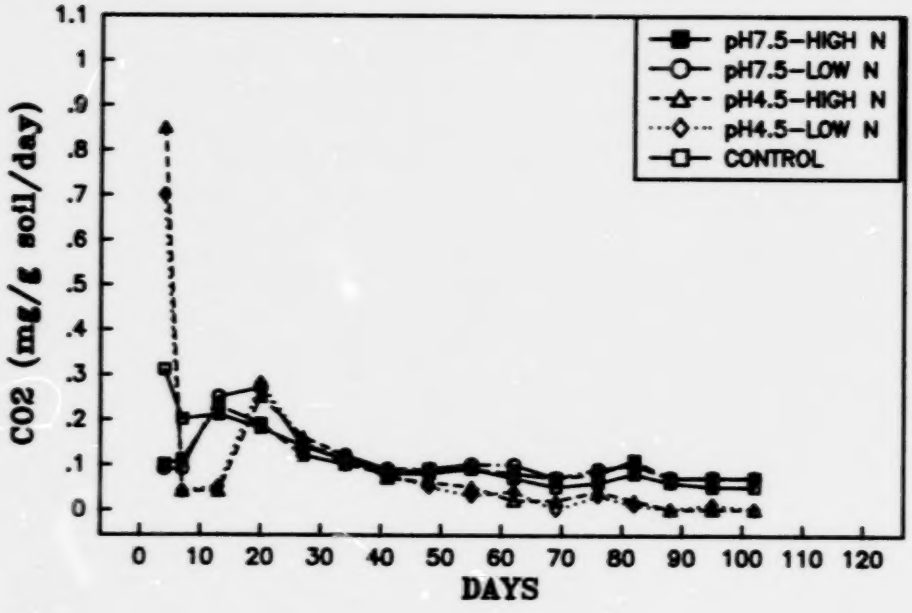
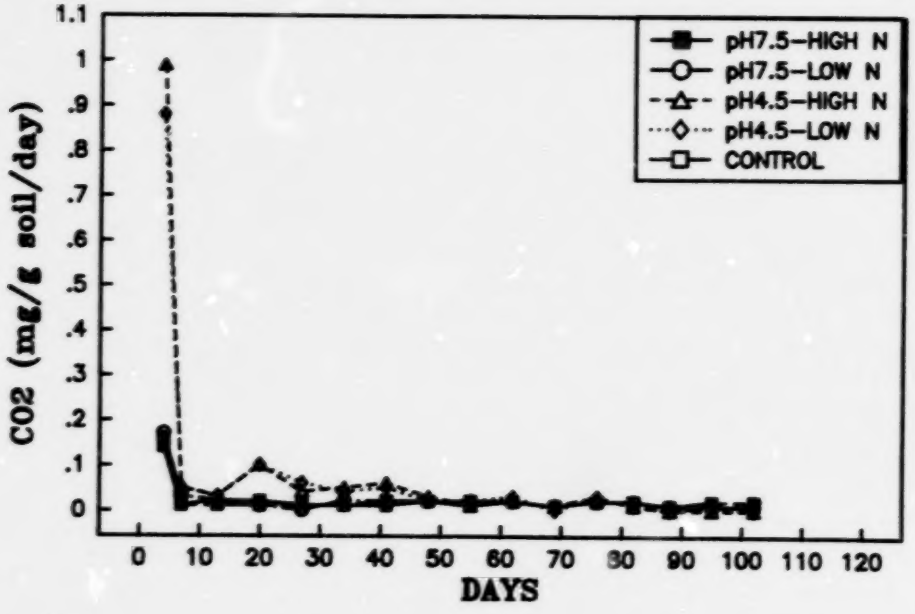


FIGURE 6.3.1.4 ANTHRACENE - RATE OF TOTAL CO_2 EVOLVED
STERILIZED SOIL



this treatment the actual pH ranged from 3.5 to 4.5. It is possible that acidophilic organisms in the soil were more tolerant of mercury.

Nutrient addition was observed to have a stimulatory effect on metabolic activity over that of the control soil which received no nutrient addition in the benzo(a)pyrene study, however no difference was observed between levels of nutrient addition. For the studies with naphthalene and anthracene, the control soil received the low level of nutrient addition, to enable assessment of the effects of PAH addition on total respiration.

The rates of total CO_2 evolution were similar for the benzo(a)pyrene and naphthalene studies, ranging from 1 - 2 mg/g soil/day for the first 30 days and dropping to 0.2 - 0.4 mg/g soil/day. Respiration during the anthracene study was lower by a factor of 10, possibly due to the longer period of storage (approximately 4 months) before the soil was used.

6.3.2 Fate of ^{14}C-Benzo(a)pyrene

The concentration of ^{14}C in the flask atmosphere was monitored weekly, throughout the incubation period, and identified as CO_2 (collected in NaOH), organic products (collected in NaOH but extracted with hexane) or parent benzo(a)pyrene (collected on plug and confirmed as benzo(a)pyrene by column chromatography). Further identification of the organic product was attempted, however the material was extremely volatile and was not retained by the chromatographic column. It was concluded that the product was somewhat polar and of low molecular weight. The cumulative ^{14}C, expressed as a per cent of the ^{14}C added, after 145 days of incubation is presented for each soil treatment in Table 6.3.2.1.

Evolution of ^{14}C into the flask atmosphere was largely a function of biological processes, as is evident from the high per cent of ^{14}C in the atmosphere with biologically active soil (0% $HgCl_2$). The majority of ^{14}C was in the form of benzo(a)pyrene metabolite. Complete mineralization of benzo(a)pyrene to CO_2 accounted for an average of about 5% of the benzo(a)pyrene added in biologically active soil. This was approximately two orders of magnitude greater than that previously observed in unacclimated soil (Bulman et al., 1985).

Analysis of variance indicated that production of both CO_2 and organic metabolite were significant in biologically active soil. Table 6.3.2.2 shows the variance (mean squares) associated with each soil treatment and interaction, as well as that for experimental error. A comparison of treatment variance with error variance (F test) indicates whether a treatment had a significant effect. Significant effects are indicated in Table 6.3.2.2 at 95 and 99% levels of confidence.

Although the treatment means in Table 6.3.2.1 suggest that evolution of CO_2, and perhaps the organic metabolite, were enhanced with the higher level of nutrient addition, the data was variable and, relative to the error variance, the effect was not significant. Likewise, the effects of pH or any treatment interactions were not significant.

Figure 6.3.2.1 illustrates the cumulative evolution of ^{14}C-CO_2 from biologically active soil, expressed as a percentage of ^{14}C added, with the high and low pH and nutrients treatments. The peak mineralization of

benzo(a)pyrene to ^{14}C-CO_2 coincided with peak total CO_2 evolution and, after a period of 70 days proceeded linearly (zero order kinetics). At a soil pH of 7.5, rates of ^{14}C-CO_2 evolution (in ^{14}C/day) were 0.0587+/-0.0094 (R^2=.9605) and 0.1154+/-0.0092 (R^2=.9911) with the low and high levels of nutrient addition, respectively. At pH 4.5, rates were 0.0776+/-0.0171 (R^2=.9240) and 0.1112+/-0.0100 (R^2=.9877) for low and high levels of nutrient addition. The rates of ^{14}C-CO_2 evolution observed with the high nutrient addition were significantly higher than with the low nutrient addition, although this effect did not result in a significant difference, as assessed by analysis of variance, in total ^{14}C-CO_2 produced.

Table 6.3.2.1 Per cent of ^{14}C applied as benzo(a)pyrene (B(a)P) and collected from components of the flask atmosphere.

TREATMENTS		^{14}C IN ATMOSPHERE			
N (mg kg-1)	$HgCl_2$ (%)	CO_2 (%)	products NaOH (%)	B(a)P (%)	Total (%)
control (pH 7.5)					
600	0	0.02	0.001	0.005	0.026
600	2	0.01	0.001	0.002	0.013
pH 4.5					
600	0	4.56	0.123	0.012	4.70
1000	0	6.21	0.145	0.016	6.37
600	2	0.02	0.002	0.008	0.03
1000	2	0.02	0.002	0.011	0.03
pH 7.5					
600	0	3.41	0.099	0.024	3.53
1000	0	7.23	0.117	0.028	7.38
600	2	0.02	0.002	0.009	0.03
1000	2	0.01	0.002	0.041	0.05

It was speculated that degradation of benzo(a)pyrene may have been influenced by the variations in moisture status, in a manner similar to total CO_2 evolution. A separate trial was set up in which soil with the high nutrient, pH 7.5 treatment was prepared and incubated under three moisture regimes; constant moisture, two wet and dry cycles and three wet and dry cycles. In all cases, the degradation of benzo(a)pyrene was similar to that observed above, suggesting that degradation of benzo(a)pyrene was not influenced significantly by the soil moisture status, but occurred following an acclimation period of approximately 70 days.

The concentrations of ^{14}C in soil were measured at the end of the incubation period and are presented in Table 6.3.2.3. The ^{14}C in soil

extract was partitioned between hexane and water. Water soluble ^{14}C was assumed to be a transformation product (Extracted Product), while hexane soluble ^{14}C was confirmed as benzo(a)pyrene by column chromatography (Extracted B(a)P). The remaining ^{14}C in soil residue was determined by combustion and could not be identified as parent benzo(a)pyrene or product.

Table 6.3.2.2 Results of analysis of variance due to soil treatments for per cent of ^{14}C applied as Benzo(a)pyrene and collected in components of the flask atmosphere (degrees of freedom = 1 for treatments, 16 for error)

Source	Variance		
	CO_2	low mw organic	B(a)P
Bioactivity (B)	15.93[b]	0.0485[b]	0.00007
pH (P)	0.003	0.0017	0.00012
Nutrient addition (N)	0.422	0.0001	0.00001
BP	0.002	0.0017	0.00028
BN	0.426	0.0001	0.00012
PN	0.054	0.0002	0.00013
BPN	0.056	0.0002	0.00003
Error	0.191	0.0015	0.00015

[b] significant at 99% confidence level

Substantial ^{14}C was found in all soil fractions, as compared to the control soil. The ^{14}C extracted as benzo(a)pyrene was similar with all soil treatments, although analysis of variance (Table 6.3.2.4) indicated that the interaction of pH and nutrient addition may be significant. With the pH 4.5 treatment there was a difference of about 5% in average extracted benzo(a)pyrene between the two levels of nutrient addition, whereas with the pH 7.5 treatment the difference was about 2%. It is doubtful, however, that the difference in response was due to changes in soil processes. Extraction of benzo(a)pyrene from soil is the most variable of the parameters measured, because of variability in recovery from the soil matrix. As a result it is a very insensitive indicator of treatment effects.

Water soluble transformation products were significantly greater in biologically active soil, suggesting that they are products of biological activity. They also tended to be greater with the high level of nutrient addition. The nutrient effect was most significant in the biologically active soil at pH 4.5, as indicated by the significant interaction between

pacy significant effect noted for ^{14}C remaining in soil residue was that of biological activity. Apparently, at least a portion of the ^{14}C in soil residue is the product of biological activity, possibly due to the incorporation of carbon into microbial biomass.

Table 6.3.2.3 Percentage of ^{14}C applied as benzo(a)pyrene (B(a)P) and collected from components of the soil

TREATMENTS		^{14}C IN SOIL				TOTAL ^{14}C
N (mg kg^{-1})	$HgCl_2$ (%)	Extracted B(a)P	Extracted Product	Residue	Total in soil	Atmosphere and soil
control (pH 7.5)						
600	0	0.00	0.1	0.005	0.11	0.14
600	2	0.00	0.1	0.012	0.11	0.12
pH 4.5						
600	0	66.75	2.1	4.71	78.25	82.95
1000	0	68.25	3.9	5.41	83.93	90.30
600	2	73.00	2.3	1.60	76.90	76.93
1000	2	81.55	2.4	1.83	85.78	85.81
pH 7.5						
600	0	83.20	3.1	4.35	90.65	94.18
1000	0	78.45	3.5	4.78	86.78	94.16
600	2	74.95	2.2	2.06	79.26	79.29
1000	2	76.20	2.7	1.88	80.78	80.83

The total recovery of ^{14}C from the biometer flasks is also shown in Table 6.3.2.3. Recovery averaged approximately 90% in biologically active soils and an average of approximately 10% of the ^{14}C applied was recovered as microbial metabolite (in soil and atmosphere). In sterilized soil, recovery averaged approximately 81%, with approximately 5% accounted for as transformation product or bound residue. The reason for the poorer recovery from sterilized soil is not known.

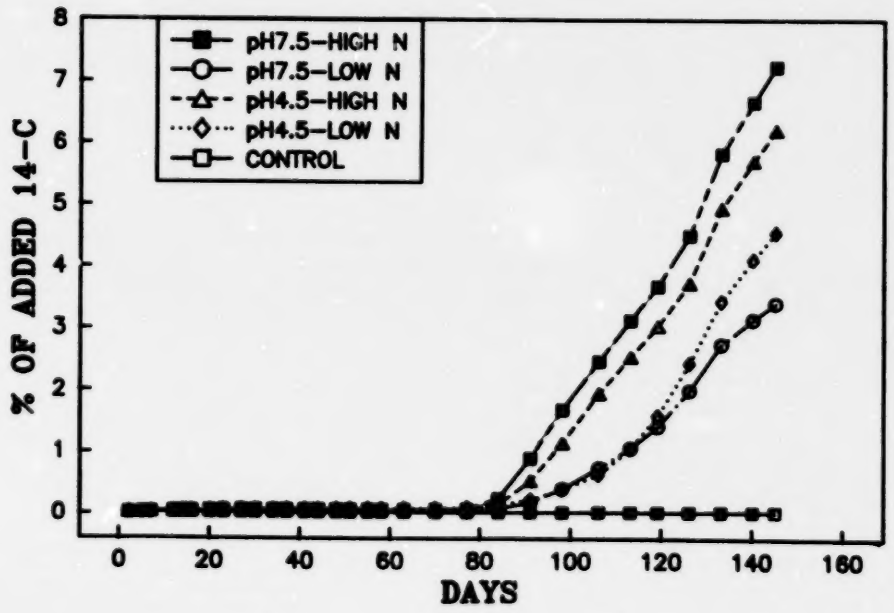
In comparison with previous studies, the results of the incubation with ^{14}C-benzo(a)pyrene indicated that degradation of benzo(a)pyrene was substantially greater in soils with a history of oily waste application than in previously uncontaminated soils. A similar period of acclimation was required, however, regardless of prior exposure, suggesting that enhanced degradation was not due to prior acclimation of the microorganisms to benzo(a)pyrene, but was due to greater numbers of microorganisms, or the greater availability of carbon substrate in the oily soil, thus increasing the potential for cometabolism of benzo(a)pyrene.

Table 6.3.2.4 Results of analysis of variance due to soil treatments for per cent of ^{14}C applied as Benzo(a)pyrene and collected in components of the soil (degrees of freedom = 1 for treatments, 16 for error)

Source	Variance		
	Extracted B(a)P	Extracted Product	Residue
Bioactivity (B)	1.281	0.324[b]	3.594[b]
pH (P)	0.518	0.015	0.088
Nutrient addition (N)	0.002	0.100[a]	0.127
BP	0.318	0.0002	0.014
BN	0.0004	0.034	0.051
PN	1.353[a]	0.035	0.055
BPN	0.254	0.073[a]	0.130
Error	0.292	0.013	0.091

[a] significant at 95% confidence level
[b] significant at 99% confidence level

FIGURE 6.3.2.1 BENZO(A)PYRENE CUMULATIVE $^{14}CO_2$, BIOLOGICALLY ACTIVE SOIL



6.3.3 Fate of Naphthalene

Table 6.3.3.1 summarizes ^{14}C collected from components of the flask atmosphere, including CO_2 (collected in NaOH), volatile organic products collected in NaOH but extracted with hexane, volatile organic products collected on the florisil cartridge (eluted with nonpolar solvent) and parent naphthalene collected on the florisil cartridge (eluted with polar solvent and verified as naphthalene). The results presented are cumulative over the 68 day period. The effects of soil sterilization, pH and nutrient treatment on loss of ^{14}C from soil are compared in Table 6.3.3.2 by analysis of variance.

A major mechanism for loss of naphthalene from the biologically active soil was mineralization to CO_2. Figure 6.3.3.1 illustrates the evolution of ^{14}C labelled CO_2 from biologically active soil over the incubation period with high and low pH and nutrient treatments. Mineralization of naphthalene proceeded immediately in the soil at pH 7.5 and was minimal after 20 days. In the soil at pH 4.5, mineralization did not occur until after a 10 day period. It was observed at the end of the incubation that the pH in the 4.5 treatment had increased to as high as 5.2. Therefore, it was not clear whether the degradation that took place after 10 days was performed by acidophilic organisms, or whether the pH had already increased, allowing the non-acidophilic microbial population to re-establish. No significant

FIGURE 6.3.3.1 NAPHTHALENE CUMULATIVE $^{14}CO_2$, BIOLOGICALLY ACTIVE SOIL

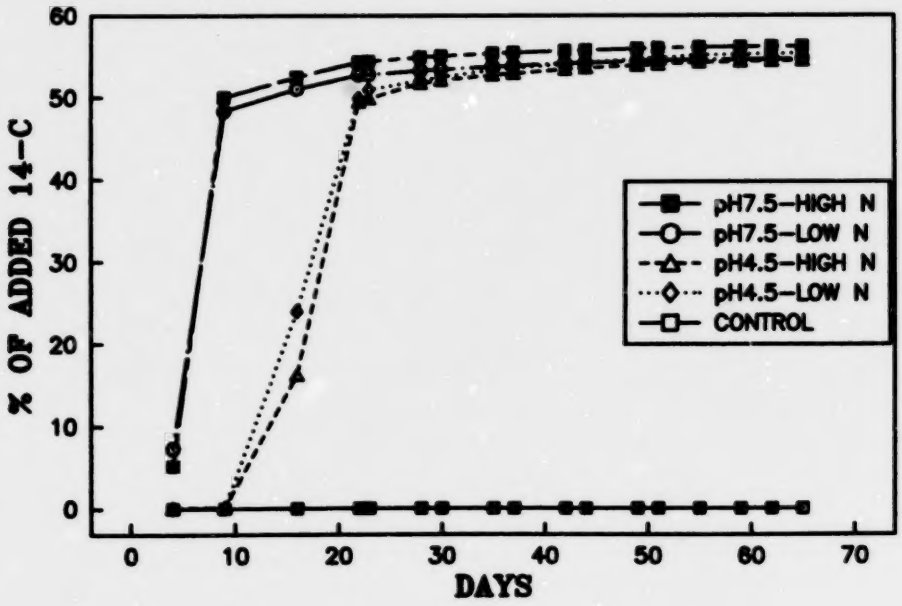


Table 6.3.3.1 Percentage of ^{14}C applied as naphthalene (Naph) and collected from components of the flask atmosphere

TREATMENTS		ATMOSPHERE				
N (mg kg^{-1})	$HgCl_2$ (%)	CO_2	Products NaOH	Products Cartridge	Naphthalene Cartridge	Total in atm.
control (pH 7.5)						
600	0	0.06	.00	0.01	.00	0.07
600	2	0.08	.00	0.01	0.01	0.10
pH 4.5						
600	0	55.36	2.34	0.02	1.25	58.97
1000	0	56.23	1.48	0.02	1.02	58.75
600	2	0.26	0.41	0.06	2.91	3.64
1000	2	0.33	0.46	0.04	2.93	3.76
pH 7.5						
600	0	57.71	0.83	0.01	0.06	58.61
1000	0	60.97	1.34	0.01	0.04	62.36
600	2	0.41	0.59	0.04	4.03	5.07
1000	2	0.28	0.43	0.03	2.53	3.27

effects on cumulative ^{14}C-CO_2 evolution were observed for pH or nutrient addition (Table 6.3.3.2). Sterilization had a significant effect, however, indicating that mineralization was the result of biological activity.

The ^{14}C was also evolved from soil as products, either collected in NaOH and extracted in hexane or collected on the florisil cartridge. Compounds collected in NaOH were volatile and water soluble, but were partitioned preferentially into hexane. Compounds collected on the cartridge were assumed not water soluble. Further identification of volatile products was not possible as they were quickly lost.

Significant amounts of the water soluble products were evolved only from biologically active soil and were likely the result of metabolic activity. The products collected on the cartridge, however, were significantly greater with the sterile treatments, suggesting that they were the result of physical/chemical reactions. The appearance of transformation products on the cartridge coincided with collection of volatilized naphthalene on the cartridge. This may have resulted from transformation of naphthalene in the cartridge after volatilization, for example through photolysis reactions. Due to the uncertainty of the pH 4.5 treatment, little confidence can be given to the interpretation of pH effects.

Volatilization of naphthalene was observed with the sterile soil, and also with the pH 4.5 treatment. Volatilization occurred predominantly in the

first 15 - 20 days. More naphthalene was volatilized from biologically active soil at pH 4.5 than at pH 7.5, likely due to the difference in mineralization of naphthalene over this period. All treatments were observed to have a significant effect on cumulative volatilization of naphthalene (Table 6.3.3.2). Due to the uncertainty of the pH 4.5 treatment, however, little confidence can be placed in the interpretation of pH effects or interaction effects involving the pH treatment. The level of nutrient addition may have had a significant effect, with volatilization of naphthalene being greatest with the low level of nutrient addition in the sterile soil. However, as the effect was observed only in the sterile treatment, it is not likely biological in nature and the reason for it is not known.

Table 6.3.3.2 Results of analysis of variance due to soil treatments for per cent of ^{14}C applied as naphthalene (Naph) and collected in components of the flask atmosphere

Source	Variance			
	CO_2	water sol. products	products on cartridge	naphthalene on cartridge
Bioactivity (B)	257.9[b]	0.745[b]	0.0022[b]	4.54[b]
pH (P)	0.0067	0.084	0.0002	0.272[b]
Nutrient addition (N)	0.0014	0.00006	0.0001	0.043[a]
BP	0.0025	0.136[a]	0.00008	0.537[b]
BN	0.0050	0.005	0.00009	0.0012
PN	0.0003	0.0007	0.0000001	0.018
BPN	0.0326	0.022	0.0000001	0.079[b]
Error	0.0751	0.028	0.00005	0.0076

[a] significant at 95% confidence level
[b] significant at 99% confidence level

The ^{14}C-CO_2 data over 0 to 10 days and 0 to 22 days for the 7.5 and 4.5 pH treatments, respectively, were fitted to an exponential (first order) equation to estimate the rate of naphthalene mineralization. Rate constants were 0.1860 +/-0.0205 (R^2 = 9834) and 0.1907 +/-0.0706 (R^2 = 0.8408) for the low and high rate of nutrient addition, respectively, in soil at pH 7.5 and 0.2008 +/-0.0382 (R^2 = 0.9302) and 0.1924 +/-0.0327 (R^2 = 0.9450) for the low and high rate of nutrient addition, respectively, in soil at pH 4.5. The rate constants did not differ significantly between treatments.

The concentrations of ^{14}C measured in soil at the end of the incubation period are presented in Table 6.3.3.3. Extracted naphthalene was identified by column chromatography, while other extracted ^{14}C-labelled

chemical was assumed to be transformation product. The remaining ^{14}C in soil residue was determined by combustion and could not be identified.

Table 6.3.3.3 Per cent of ^{14}C applied as naphthalene (Naph) and collected from components of the soil

TREATMENTS		SOIL				TOTAL ^{14}C
N ($mg\ kg^{-1}$)	$HgCl_2$ (%)	Extracted Naph	Extracted Product	Residue	Total in soil	Atmosphere and soil
control (pH 7.5)						
600	0	0.04	0.03	0.01	0.08	0.15
600	2	0.04	0.03	0.02	0.09	0.19
pH 4.5						
600	0	0.86	0.52	14.92	16.30	75.27
1000	0	0.82	0.42	12.66	13.90	72.65
600	2	70.17	0.36	0.29	70.82	74.46
1000	2	69.53	0.39	0.25	70.17	73.93
pH 7.5						
600	0	0.45	0.36	19.17	19.98	78.59
1000	0	0.47	0.34	12.45	13.26	75.62
600	2	76.00	0.46	0.33	76.79	81.86
1000	2	53.84	0.30	0.28	54.42	77.69

The concentration of naphthalene in biologically active soil had been reduced by approximately 99%, with 10 to 20% of it being incorporated into unextractable residue. The residual ^{14}C may have been either naphthalene or transformation products. As the residue was associated with biological activity, however, it is likely that it was incorporated into microbial biomass. The majority of ^{14}C recovered from sterile soil was in the form of extractable naphthalene. Small amounts of extractable products were observed with all treatments.

The effects of soil treatments are compared in Table 6.3.3.4 by analysis of variance. Biological activity had a significant effect on extractable naphthalene and unextractable ^{14}C residue which was consistent with that observed for CO_2 evolution. Sterilization by $HgCl_2$ inhibited formation of the unextractable residue and resulted in little loss of naphthalene from soil. Loss of naphthalene from sterile soil was primarily through volatilization. Biological activity apparently resulted in transformation of naphthalene to CO_2 and microbial biomass. Naphthalene was labelled on one of the two rings (1 position) in this study, and was converted to either CO_2 or biomass according to a ratio of approximately 1:4.

Table 6.3.3.4 Results of analysis of variance due to soil treatments for per cent of ^{14}C applied as naphthalene (Naph) and collected in components of the soil

Source	Variance		
	Extracted Naph	Extracted Product	Residue
Bioactivity (B)	317.5[b]	.00002	54.57[b]
pH (P)	0.568[a]	0.0070[a]	0.014
Nutrient addition (N)	0.764[b]	0.0037	0.610[b]
BP	0.111	0.0043	0.009
BN	0.782[b]	0.0001	0.513[b]
PN	0.208	0.0009	0.050
BPN	0.261	0.0091[a]	0.027
Error	0.076	0.0012	0.023

[a] significant at 95% confidence level
[b] significant at 99% confidence level

Nutrient addition also had a significant effect on extractable naphthalene and unextractable residue. The high levels of nutrient addition resulted in less ^{14}C recovered in the unextractable fraction in biologically active soil, and also in the extractable naphthalene fraction of sterile soil, leading to reduced overall recovery. It appears most likely that the nutrient addition resulted in an unexplained reduction in the recovery of ^{14}C, rather than on transformation processes.

Soil pH may have had a significant effect on extractable naphthalene and products, however as the actual efficiency of the pH treatment was not clear, little confidence can be placed on the interpretation of pH effects or pH interaction effects.

Total recovery of ^{14}C was not as good as in the other studies and was attributed to losses during analysis as a result of the high volatility of naphthalene. Recovery of approximately 76% (+/-3%) and 77% (+/-4%) were observed for biologically active and sterile soil, respectively. Losses measured in flask rinses and on the rubber stoppers were less than 0.5%.

6.3.4 Fate of Anthracene

The ^{14}C in the flask atmosphere was identified as CO_2 (collected in NaOH), organic products collected in NaOH (extracted with hexane), organic products collected on the cartridge (eluted with a polar solvent) or parent anthracene (collected on the cartridge but eluted with a nonpolar solvent and verified as anthracene). As observed previously for benzo(a)pyrene and naphthalene, the organic products were too volatile to be identified by column chromatography. The cumulative ^{14}C, expressed as a percentage of the ^{14}C added, after 107 days of incubation, is presented for each soil treatment in Table 6.3.4.1.

Table 6.3.4.1 Percentage of ^{14}C applied as anthracene and collected from components of the flask atmosphere

TREATMENTS		ATMOSPHERE				
N (mg kg^{-1})	$HgCl_2$ (%)	CO_2	Products NaOH	Products Cartridge	Anthracene Cartridge	Total in atm.
control (pH 7.5)						
600	0	0.06	0.01	0.02	0.03	0.12
600	2	0.05	0.02	0.02	0.02	0.11
pH 4.5						
600	0	0.08	0.02	0.03	0.04	0.17
1000	0	0.09	0.03	0.03	0.05	0.20
600	2	0.04	0.02	0.03	0.03	0.12
1000	2	0.04	0.02	0.03	0.05	0.14
pH 7.5						
600	0	26.50	2.54	0.03	0.03	29.10
1000	0	24.58	2.36	0.02	0.03	26.99
600	2	0.05	0.04	0.04	0.03	0.16
1000	2	0.03	0.01	0.03	0.03	0.10

The results suggested that the only emission from soil of anthracene or its products occurred as CO_2 or low molecular weight polar products. The high per cent of these products evolved from biologically active soil (0% $HgCl_2$) indicated that they occurred as a result of biological activity. Complete mineralization to CO_2 accounted for approximately 25% of anthracene added to biologically active soil at pH 7.5, and approximately 2% was evolved as a low molecular weight, volatile intermediate. Mineralization of anthracene did not occur at pH 4.5, although the soil was not actually sterilized (Figure 6.3.1.3). This suggests that the organisms capable of

completely degrading anthracene required a pH greater than 4.5 for survival (i.e. were not acidophiles).

The effects of soil sterilization, pH and nutrient addition are compared in Table 6.3.4.2 by analysis of variance. The effects of both biological activity and soil pH on the production of ^{14}C-CO_2 and polar metabolites were significant at the 99% level of confidence. The effect of sterilization by $HgCL_2$ addition was only apparent in soil at pH 7.5 (indicated by significant bioactivity X pH interaction) as the production of ^{14}C-CO_2 and other metabolites was inhibited at pH 4.5. The level of nutrient addition had no significant effect on anthracene degradation.

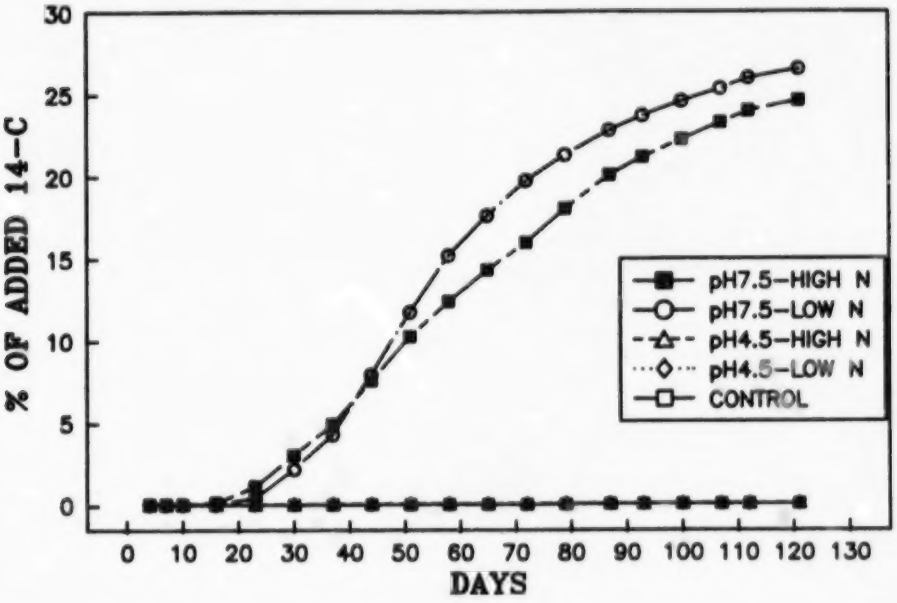
Table 6.3.4.2 Results of analysis of variance due to soil treatments for per cent of ^{14}C applied as anthracene and collected in components of the flask atmosphere (degrees of freedom = 1 for treatments and interactions, 16 for error).

Source	Variance			
	CO_2	water sol. products	products on cartridge	anthracene on cartridge
Bioactivity (B)	28.93[b]	1.456[b]	0.000069	0.000000001
pH (P)	28.23[b]	1.468[b]	0.000030	0.000273
Nutrient addition (N)	0.014	0.002	0.000069	0.000189
BP	28.21[b]	1.435[b]	0.000031	0.000000001
BN	0.010	0.0002	0.000009	0.000008
PN	0.015	0.002	0.000030	0.000067
BPN	0.013	0.0003	0.000032	0.000008
Error	0.008	0.009	0.000075	0.000078

[b] significant at 99% confidence level

Figure 6.3.4.1 illustrates the cumulative evolution of ^{14}C-CO_2 from soil, expressed as a percentage of ^{14}C added for the low and high pH and nutrient treatments. In soil at pH 7.5, mineralization of anthracene appears to follow an S-shaped growth curve, suggesting a period of acclimation occurred, followed by exponential growth of anthracene degrading organisms and a gradual decline in growth rate as availability of substrate declined. This interpretation is supported by the low concentration of anthracene detected in soil after the 121 day incubation. The evolution of organic products collected in hexane coincided with that of ^{14}C-CO_2 evolution. The ^{14}C-CO_2 data for soil at pH 7.5, was fitted to both linear (zero order) and exponential (first order) models to estimate the rate of anthracene mineralization.

FIGURE 6.3.4.1 ANTHRACENE - CUMULATIVE $^{14}CO_2$, BIOLOGICALLY ACTIVE SOIL



An exponential model fit the data over the first 37-day period (growth phase) with rate constants of 0.1521+/-0.0228 (R^1=.9082) and 0.1477+/-0.0177 (R^2=.9389) for the low and high levels of nutrient addition, respectively. For the remaining 44 to 121-day period (decline phase) an inverse exponential model fit with rate constants of -0.0045+/-0.0009 (R^2=.7844) and -0.0055+/-0.0012 (R^2=.7448) for the low and high levels of nutrient addition respectively. Thus the S-curve is not symmetric about its point of inflection, and the decline phase is likely a higher order reaction. No significant difference in the rate constants was observed between nutrient levels. The growth phase rate constants appeared lower than those observed for naphthalene, but the differences were not significant.

Omitting the first 15 days as acclimation period, the linear model fit over the 15 to 121-day period with rates of 0.2858+/-0.0229 (R^2=.9272) and 0.2548+/-0.0204 (R^2=.9365) for the low and high levels of nutrient addition, respectively. Although this model fit the data adequately over the period of this study, it is likely that a further decline in ^{14}C-CO_2 evolution would occur over a longer period, resulting in a poorer fit of the linear model. No significant difference in rates was observed between nutrient levels. The linear rates were significantly higher than those observed for benzo(a)pyrene.

The concentrations of ^{14}C in soil were measured at the end of the incubation period and are presented in Table 6.3.4.3. Extracted anthracene was identified by column chromatography, while other extracted ^{14}C-labelled chemical was assumed to be a transformation product. The remaining ^{14}C in soil residue was determined by combustion and could not be identified.

Table 6.3.4.3 Per cent of ^{14}C applied as anthracene (Anth) and collected from components of the soil

TREATMENTS		SOIL				TOTAL ^{14}C
N (mg kg^{-1})	$HgCl_2$ (%)	Extracted Anth	Extracted Product	Residue	Total in soil	atmosphere and soil
control (pH 7.5)						
600	0	0.13	0.05	0.03	0.21	0.32
600	2	0.06	0.03	0.16	0.25	0.36
pH 4.5						
600	0	74.76	10.36	3.65	88.77	88.94
1000	0	72.23	9.94	7.94	90.11	90.31
600	2	79.79	7.44	2.43	89.66	89.78
1000	2	75.13	9.18	3.04	87.35	87.49
pH 7.5						
600	0	2.17	7.30	72.76	82.23	111.33
1000	0	1.64	5.49	71.74	78.87	105.86
600	2	92.32	8.61	1.65	102.58	102.74
1000	2	85.90	8.44	1.15	95.49	95.59

The results suggest that at pH 7.5, biological degradation reduced the concentration of extractable anthracene in the soil by approximately 98%, with much of it (approximately 72%) being incorporated into the soil solid phase in an unextractable form. The unextractable ^{14}C-labelled residue may have been either anthracene or metabolic products. As it is associated with biological activity, however, it is most likely that it consists of ^{14}C which has become incorporated into microbial biomass as a result of anthracene degradation. Small amounts of unextractable ^{14}C residue were also observed at pH 4.5 and in sterilized soil, and extractable polar products were observed with all treatments.

The effects of the soil treatments are compared in Table 6.3.4.4 by analysis of variance. Bioactivity and soil pH had significant effects on extractable anthracene and unextractable ^{14}C residue which were consistent with that observed for ^{14}C-CO_2 evolution. Both sterilization by $HgCl_2$ addition and pH 4.5 inhibited formation of the unextractable residue and resulted in little loss of anthracene from soil. It is apparent that biological activity was responsible for removal of anthracene from soil by converting it into CO_2 and biomass. The labelled carbon on the anthracene molecule was on the centre ring (9 position) and in this study was converted into CO_2 or biomass according to a ratio of approximately 1:4.

Table 6.3.4.4 Results of analysis of variance due to soil treatments for per cent of ^{14}C applied as anthracene (Anth) and collected in components of the soil (degrees of freedom = 1 for treatments and interactions, 16 for error).

Source	Variance		
	Extracted Anth	Extracted Product	Residue
Bioactivity (B)	99.49[b]	0.0057	90.44[b]
pH (P)	61.83[b]	0.6333[b]	48.53[b]
Nutrient addition (N)	0.32[a]	0.0263	0.265
BP	88.80[b]	0.8021[b]	64.29[b]
BN	0.028	0.2314	0.295
PN	0.005	0.1050	0.693
BPN	0.001	0.0047	0.147
Error	0.039	0.0546	0.162

[a] significant at 95% confidence level
[b] significant at 99% confidence level

A significant effect was also observed for nutrient addition on extractable anthracene with all treatments. Somewhat less anthracene was extracted from soil with the high level of nutrient addition than from that with low nutrient addition. Correspondingly higher levels of transformation products were not observed, however, suggesting that there was an effect of nutrient addition on the recovery of anthracene by extraction, rather than on transformation processes.

The concentration of extractable transformation products was also affected significantly by soil pH, with the effect evident only in biologically active soil (significant bioactivity X pH interaction). Some polar products were apparently produced in sterile soil, presumably by physical and chemical processes. In biologically active soil, these products accumulated to a greater degree at pH 4.5, whereas at pH 7.5 fewer polar products accumulated. The results suggest that a neutral soil pH is required for the most complete degradation of anthracene in soil.

Total recovery of ^{14}C from the biometer flasks averaged approximately 99% (+/-11%) in biologically active soil and 94% (+/-7%) in sterilized soil. Recovery was somewhat higher at pH 7.5. Losses measured in flask rinses and on rubber stoppers were less than 0.5% .

In comparison with previous studies, degradation of anthracene in the oily soil was greater than that in previously uncontaminated soil (Bulman et al., 1985) by a factor of 400. A period of acclimation was required for

degradation in both soils. Greater numbers of microorganisms or greater availability of substrate may have induced the enhanced degradation of anthracene in the oil contaminated soil.

6.3.5 Discussion of biometer flask study results

The use of ^{14}C-labelled chemicals proved to be a useful technique for identifying the mechanisms of PAH loss from soil during incubation in flasks. In this study the technique was used to provide data using previously acclimated, oil treated soil for comparison with previously obtained data with unacclimated soil (Bulman et al., 1985) and for an assessment of the effects of soil pH and nutrient addition. It was observed that soil with a history of oily waste treatment was capable of more effective treatment of the PAH's studied than was previously observed for the unacclimated soil. Incorporation of carbon from the PAH molecule into microbial biomass also appeared to be more significant with the acclimated soil.

The technique of using ^{14}C-labelled PAH provides a more precise estimation of the degradation of PAH in soil than incubation studies relying on conventional extraction and analysis. Extraction of the chemical from soil is highly variable, but measurement of evolved CO_2 and bound residue is not. This study confirmed that benzo(a)pyrene was degraded in soil from site C, although an extensive acclimation period was required. Substantial degradation of benzo(a)pyrene in a field situation may not be observed within one landfarm field season in temperate, subhumid climatic conditions, however, as the effective length of the field season may be insufficient for both acclimation and degradation.

The techniques used to control soil pH in this study were not very successful and did not result in a satisfactory evaluation of the effects of pH on PAH degradation. Nutrient addition, at the levels applied in this study, did have a beneficial effect on overall microbial activity, but did not have a clear effect on PAH degradation.

7 CONCLUSIONS AND RECOMMENDATIONS

Three general approaches to studying the fate of PAH's were used in the course of this research program. Two approaches involved laboratory activities, namely the incubations using ^{14}C-labelled chemicals in biometer flasks and the incubations in which the concentrations of 16 indigenous PAH's were monitored. The third approach was the monitoring of PAH concentrations in soil and water at a field site. The laboratory studies were intended to provide more detailed and precise information than could be obtained from a field study. The method of using ^{14}C-labelled chemicals provided the most information regarding the fate of the chemical studied, for example, the proportions degraded, volatilized and incorporated into soil organic matter. The results of the studies with ^{14}C were also more precise than those in which non-labelled chemicals were monitored. For determination of the persistence of all PAH isomers in a refinery waste, however, the ^{14}C technique would be prohibitively expensive, due to the high cost and lack of availability of labelled compounds.

The approach of monitoring the concentrations of waste constituents in soil over time, as performed in the kinetic incubation study and the field program, is commonly used in environmental studies. The oily waste matrix used in this study presented severe analytical difficulties. As a result, soil analyses in the incubation study and the field program were generally inconclusive. Analysis of the large number of samples was also costly and labour intensive. A similar incubation study performed previously with pure chemicals, (Bulman et al., 1985) produced more precise results and was useful in predicting the relative rates of degradation of PAH's. The study with oily waste demonstrated that substantial methods development for the analysis of oily samples is required for routine assessment of PAH concentrations in landfarm soil. In addition, the study highlighted the need for extensive sample replication and a good quality assurance program, including adequate evaluation of sampling and analytical variability, in monitoring of PAH concentrations in oily waste treated soil. The possibility of variable recovery of PAH's from samples must be considered as part of the analytical program. These considerations are important for research studies as well as for monitoring during the operation and decommissioning of field sites.

In spite of the limitations on the precision and accuracy of the field data, it was apparent from this study that some landfarming operations in 1985 contributed to an accumulation in soil of PAH's, and on one site of total oil and grease. While degradation of high molecular weight PAH's was shown to occur, substantial degradation (at least 50%) did not occur within a 200 day monitoring period. Of the 16 PAH's measured in this study, the following 8 PAH's were consistently elevated in landfarm soils as compared to background levels; phenanthrene, fluoranthrene, pyrene, chrysene, benzo(a)pyrene, benzo(a)anthracene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene.

A comparison of the three sites in this study suggested that accumulations of PAH's and, in some cases, oil and grease in landfarm soil coincided with elevated PAH and dissolved organic carbon concentrations in groundwater near the landfarm sites. Anthracene and chrysene were the PAH's most commonly measured at elevated concentrations, although concentrations of

phenanthrene, fluoranthrene, pyrene, benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were also elevated at some sites. It was observed that the concentrations in groundwater adjacent to one landfarm were less than those associated with a downstream sewage trunk line and, in comparison with overall environmental loadings, may not be significant. The environmental significance of the PAH concentrations observed in soil and groundwater was not assessed in this study. Such information is required, however, to determine appropriate soil and water quality criteria. Biological testing of groundwater and soil leachate may provide additional information on environmentally acceptable PAH concentrations in soil and water.

On the basis of observations made in this research program the following areas are recommended for future research:

1) Identification of concentrations of PAH's in soil and water which can be tolerated without detriment to health and the environment. Acceptable levels of PAH's may be dependent on soil type and other site-specific factors.

2) Improvement of routine methods of analysis for waste constituents in an oily matrix.

3) Identification of a) the period of time required to degrade high molecular weight PAH's under field conditions and b) site management methods which will increase the rates of degradation.

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GLOSSARY

acidophiles - organisms that live at low pH

asphaltenes - high molecular weight constituents of asphaltic bitumens which are soluble in carbon disulphide but not in petroleum spirit

biomass - the living mass of a population, such as the microbial population in soil

biosludge - solid or semi-solid residue resulting from biological wastewater treatment

cometabolism - metabolism of two substrates, one of which is more easily metabolized and provides a source of carbon and energy

deuterated - having constituent hydrogen atoms replaced by deuterium, an isotope of hydrogen having one proton and one neutron in the nucleus ("heavy" hydrogen)

radiolabelled - having constituent atoms replaced by radioisotopes, for example having natural carbon (^{12}C) replaced by ^{14}C

landfarm - an area of land dedicated to the disposal of waste through periodic spreading of waste on the soil surface and incorporating it into the soil

leachate - water which has percolated through a porous media and thus contains dissolved constituents from that media

photolysis - breakdown of a molecule as the result of the adsorption of light

humid - with a very slight water deficit during a field season (water deficit of 2.5 6.5cm).

unacclimated - without adjustment (in physiology) in response to a changed environment, for example without the required enzymatic activity to use a new substance as a metabolic substrate

APPENDIX A

ANALYSIS OF PAH'S IN REFINERY WASTE TREATED SOIL

ANALYSIS OF LAND FARM SOILS FOR PAH

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2.0 METHODOLOGY

2.1 Cleanup

The samples were subjected to a clean-up using gel permeation chromatography in order to remove potential interferents. The samples were subjected to solvent exchange with methylene chloride and taken to a final volume of 5 mL. They were then diluted to 10 mL using cyclohexane. Each sample was then spiked with two deuterated surrogate standards, $^{2}H_{10}$-anthracene and $^{2}H_{12}$ benzo(a)pyrene at 10 ug. Half of the sample was injected into the GPC system using the following conditions.

Column:	50 g Biobeads SX-3
Solvent:	Cyclohexane: Methylene Chloride 1:1
Flow Rate:	5 mL/min.
Pressure:	5 psi
Collect:	35-59 min.

The collected eluent was roto-evaporated to a low volume, quantitatively transferred to a centrifuge tube and evaporated in a gentle stream of nitrogen to a final volume of 1 mL for GC/MS analysis.

2.2. GC/MS Analysis

The samples were spiked with $^{2}H_{10}$ phenanthrene as an internal standard prior to injection for GC/MS analysis under the following conditions.

2.1.2.1 Gas Chromatography

Injection Mode	Splitless
Column	30 m DB5 x 0.25 mm ID
Column Flow	He @ 20 cm/sec.

Oven Temp. Profile

80°C - 2 min.;

80°C -- 210°C @ 10°/min; 210°C --- 300°C @ 16°C/min.

hold 10 min.

GC/MS Interface - Direct Couple

Transfer Area - 250°C

2.1.2.2 Mass Spectrometry

Ionization Mode	Electron Impact
Electron Energy	70 eV
Filament Emission	0.5 A
Electron Multiplier	2000 V
Scan	50-550 amu; 0.9 scans/sec.

2.2 Quantification

The compounds of interest and the quantification ions used are presented below with the secondary ion given in brackets.

Compound	Quantification Ion
Naphthalene	128
Acenaphthylene	152
Acenaphthene	154
Phenanthrene	178

Anthracene	178
Fluoranthene	202 (101)
Pyrene	202 (101)
Chrysene	228 (114)
Benz(a)anthracene	228 (114)
Benzo(b)fluoranthene	252 (126)
Benzo(k)fluoranthene	252 (126)
Benzo(a)pyrene	252 (126)
Indeno(1,2,3-c,d)pyrene	276 (138)
Dibenzo(a,h)anthracene	278 (139)
Benzo(g,h,i)perylene	276 (138)

Quantification was carried out by comparing mass spectrometric responses of selected ions to those of external standards. Calculations were based on the total amount of material in the extract and no correction has been made for recovery of deuterated surrogate spikes.

The critera used for the identification of the organics required:

a) the presence of appropriate secondary ions in the mass spectrum

b) signal to noise of at least 3 to 1

c) retention time within 2% of reference standard

4.0 QUALITY ASSURANCE

Quality control measures were taken in this work for both the sample preparation, gas chromatographic and mass spectrometric areas and are as follows:

i) Samples were received and immediately refrigerated to preserve sample integrity.

ii) Mass assignments for ions generated by GC/MS were determined from a calibration of an FC43 perfluorohydrocarbon mixture.

iii) Two surrogate spikes were added for the analytes of interest prior to GPC.

Anthracene - $^{2}H_{10}$; benzo(a)pyrene $^{2}H_{12}$

iv) Addition of internal standards sample extracts just prior to analysis, phenanthrene - $^{2}H_{10}$

v) Method blank performed for all analyses to correct for laboratory contamination.

vi) Criteria for identification required a) the presence of secondary ions in the mass spectrum; b) signal noise of at least 3 to 1; c) retention time within 2% of reference standard.

APPENDIX B

QUALITY ASSURANCE/CONTROL PROGRAM

QUALITY ASSURANCE/CONTROL PROGRAM

The purpose of a quality assurance/control program is to evaluate experimental data according to precision and accuracy. A program of duplicated sample analysis for PAH's was employed throughout this study to evaluate sample variability, analytical recovery and variability between analytical subsamples.

Soil sample variability was assessed through the collection and analysis of triplicate samples in the field program and by preparation and analysis of triplicate treatments in the laboratory studies. Sample variability was observed to be high where incorporation of oily was into soil was involved. The program might have benefited from additional replication, however the cost of analysis prohibited analysis of additional samples. The results of triplicate soil samples are presented in the body of the report. True sample variability was not assessed for groundwater samples as replicate piezometers were not installed.

For soil analysis, an 8 gram subsample was taken from a 50 gram replicate sample. Subsample variability and analytical recovery were assessed by taking two (duplicate) 8 gram subsamples from selected replicate samples. In some cases surrogate chemicals were added to duplicate subsamples prior to sample extraction to make "spiked" duplicates. Spiked duplicates were analysed to determine the recovery of spiked surrogate chemicals. Non-spiked duplicates were analysed to determine variability between subsamples. In addition, all sample extracts were spiked with deuterated surrogate chemicals prior to cleanup and analysis by GC/MS to evaluate analytical recovery and variability due to interference with other chemicals.

The results of analytical quality assurance and control are presented separately for each phase of the research program.

Part 1

Four out of the 42 soil samples were prepared as spiked duplicates through addition of a solution of 16 PAH's at levels ranging from 1 to 30 mg/kg, depending on the PAH. Three of the four spiked duplicates were for the 2% oil in soil treatment and the fourth was for control soil.

Recovery in general was poor, as illustrated in Figures B1.1 to B1.4. Recovery also varied unpredictably from sample to sample and for the different PAH chemicals, indicating that very little confidence can be placed in the concentrations obtained for those samples without estimates of recovery. Although the oily waste matrix undoubtedly was responsible for interference in analysis of oily waste treated samples, recovery was also poor for non-treated control soil. It would have been desirable to increase the number of samples which were duplicated and spiked, to provide additional information on samples collected throughout the incubation period. It would also be necessary to prepare triplicate or quadruplicate spiked samples to provide an estimate of subsample variability in recovery data. The use of spiked surrogate recovery data in this way assumes that surrogate recovery is representative of

indigenous chemical recovery, which may not be valid. A more satisfactory method of evaluating analytical performance is not currently available.

Part 2

Two out of 50 soil samples were prepared as spiked duplicates through addition of a solution of 10 PAH's at a level of 14 mg/kg for each PAH. An additional two samples were prepared as non-spiked duplicates. Two deuterated PAH's (d10 anthracene and d12 benzo(a)pyrene) were added to extracts of each sample prior to cleanup. Deuterated surrogates provided an estimate of recovery from the oily waste/soil matrix following sample cleanup. Spiked surrogates provided an estimate of PAH recovery including the sample extraction step as well as cleanup. Non-spiked duplicates provided an estimate of subsample variability.

Site A

Average recoveries and standard deviations for deuterated surrogates are illustrated in Figure B2.1. Although average recoveries look very good, ranging from 60 to 100%, recoveries for individual samples ranged from 20 to 165%. This range is not unusual for a complex sample such as waste in soil and is comparable to those observed in Part 1. The two deuterated PAH's selected for addition provide an opportunity to compare recovery of the high and low molecular weight range PAH's. Although the proportion of high molecular weight PAH's in soil (including benzo(a)pyrene) was observed to increase in the later incubation periods (Figure 6.2.1.1.1), it can be seen from Figure B2.1 that this effect could not be attributed to an increase in recovery during cleanup and detection. It may have resulted from an increase in recovery from the soil by extraction.

Extraction efficiency as assessed by spiked duplicates was not performed using Site A soil samples. Results using samples from the other sites indicated a decrease in extraction efficiency over the monitoring period, rather than an increase. Extraction efficiencies obtained for one soil, however, are not necessarily indicative of those obtained for another soil.

Non-spiked duplicates provided an assessment of subsampling variability. Standard deviations ranged to 28% of the mean for most PAH in duplicate samples, however, benzo(b/k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene and dibenzo(a,h)anthracene were not consistently detected in samples and varied to 100% of the mean.

Site B

Average recoveries and standard deviations for deuterated PAH's are presented in Figures B2.2a and b. Recoveries were typical (31% to 148%) with the exception of the June sample for replicate 2 (5% anthracene, 32% benzo(a)pyrene). For the samples on this site, the increase in high molecular PAH's appeared to coincide with an increase in the recovery of the high molecular weight benzo(a)pyrene.

Extraction efficiency was assessed by analysing spiked duplicate samples and ranged from 0 to 100%. Variability within duplicate samples was not assessed with site B samples, however it was found to be high in samples

from sites A and C and may have contributed to the wide variation in extraction efficiencies.

Site C

Recovery of deuterated PAH's (averaged for three replicates) are illustrated in Figure B2.3. Recoveries from the sandy soil at site C were higher than for the clay soil at site A. Average recoveries ranged from 100 to 125% with individual recoveries ranging from 60 to 160%. Extraction efficiencies, assessed by analysing spiked duplicate subsamples, were good, ranging from 74 to 111%. Variability between unspiked duplicates was high, however, ranging from 40 to 100% of the mean, with detection of naphthalene, anthracene, chrysene and benzo(a)anthracene being inconsistent among subsamples.

Detection limits for PAH's were 0.08 mg/kg in soil and waste samples (analysed by GC/MS). Detection limits for PAH's in groundwater, analysed by HPLC, are illustrated in Figure B2.4.

Part 3

Recovery of ^{14}C-labelled chemical was assessed by comparing the total ^{14}C recovered with the amount added. Recovery in these studies was generally good, although somewhat reduced with the highly volatile naphthalene and in some cases with the sterilized treatments. Variability between replicates was particularly poor for the component of ^{14}C extracted from soil. Variability and total recovery are discussed in the body of the report. Analysis of ^{14}C was not hampered by interference of co-eluants, as was the case for non-labelled chemicals in Parts 1 and 2.

Recommendations

The data obtained through sample extraction and analysis in this study were poor in both precision and accuracy. Increased sample replication may have improved precision, however at substantial cost. As subsample variability appeared to have contributed substantially to poor precision, efforts to reduce subsample variability, for example by taking larger subsamples or by analysing the entire replicate sample, may have resulted in improved precision.

The research program would have benefited from a more intensive quality assurance monitoring program. In particular, increasing the number of samples which were duplicated and spiked would have provided additional information on samples collected throughout the monitoring period. Triplicate or quadruplicate spiked samples would have been useful to provide an estimate of subsample variability in recovery data. At this time there appears to be no method for assessing analytical accuracy (specific to the sample matrix) which is preferable to the recovery of spiked surrogates.

The quality assurance program used in the performance of this study was intended primarily to document the precision and accuracy of data obtained. The analytical methods used in this study were typical of those currently accepted and routinely used for PAH analysis in solid matrices. Additional development is required for methods of PAH analysis in a

complex oily waste matrix, however, to address the problems identified through quality assurance monitoring and improve the quality of data.

FIGURE B 1.1 RECOVERY OF TWO-RING PAH'S IN WASTE TREATED SOIL

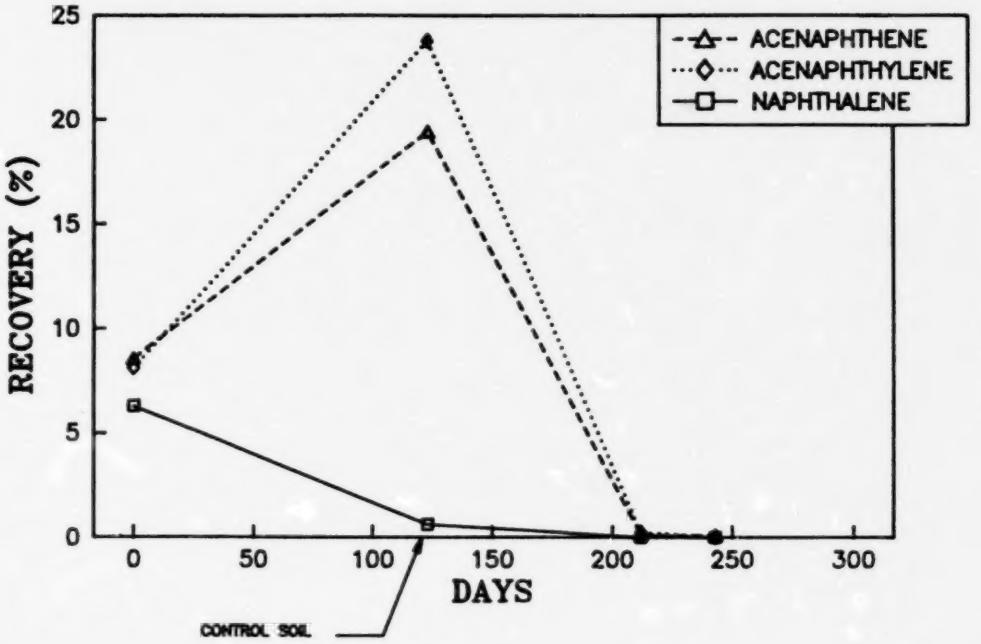

FIGURE B 1.2 RECOVERY OF THREE-RING PAH'S IN WASTE TREATED SOIL

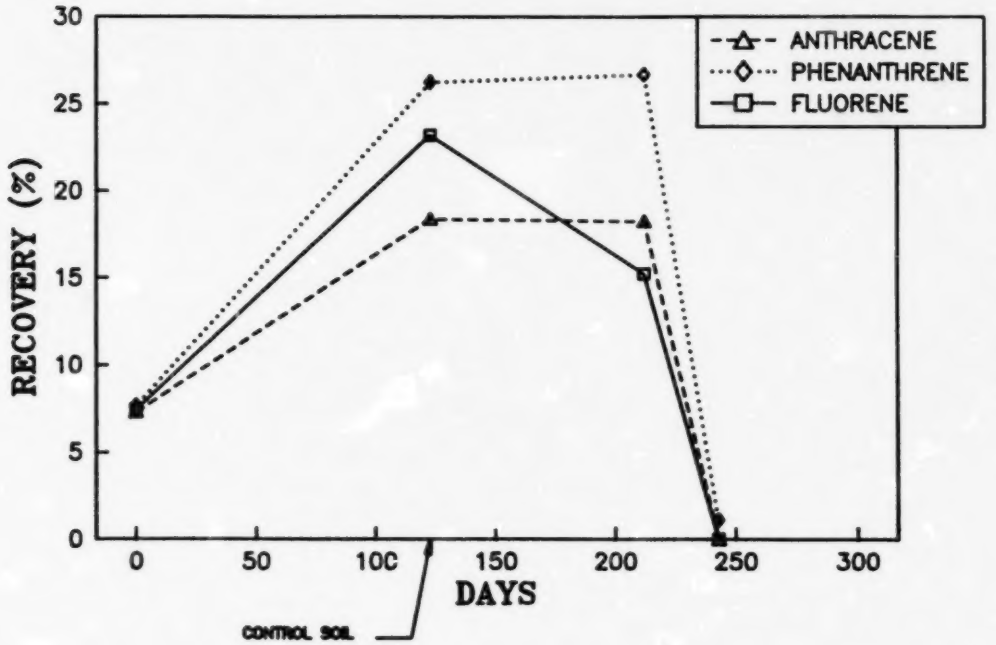

FIGURE B 1.3 RECOVERY OF FOUR-RING PAH'S IN WASTE TREATED SOIL

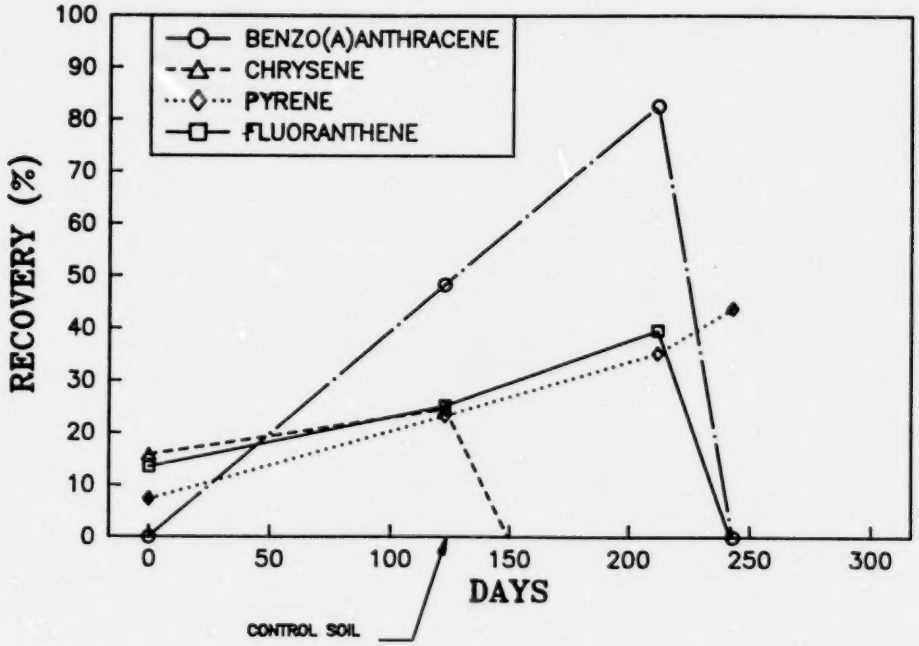

FIGURE B 1.4 RECOVERY OF FIVE TO SIX-RING PAH'S IN WASTE TREATED SOIL

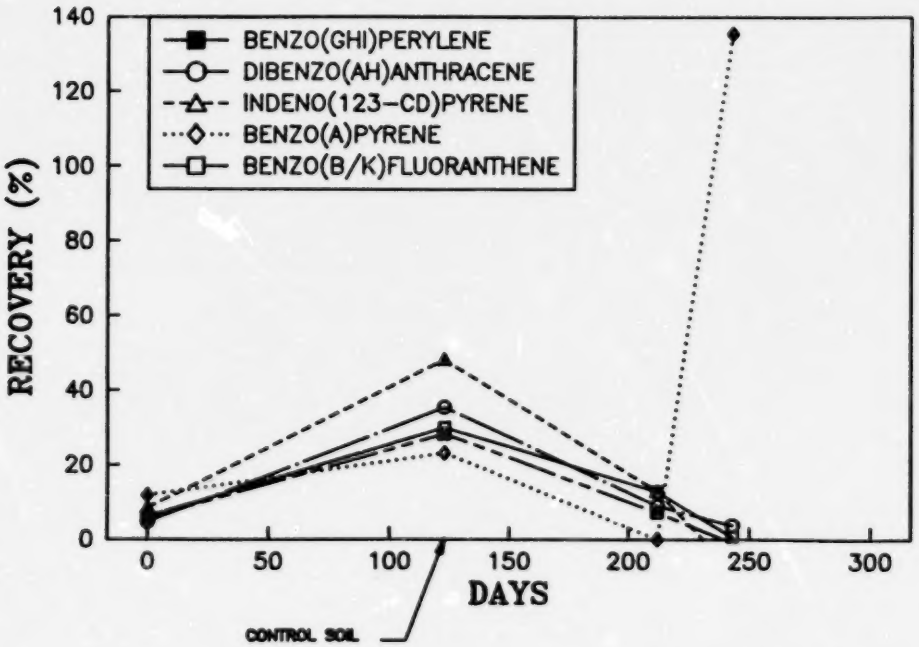

FIGURE B 2.1 RECOVERY OF PAH'S IN SITE A TOPSOIL

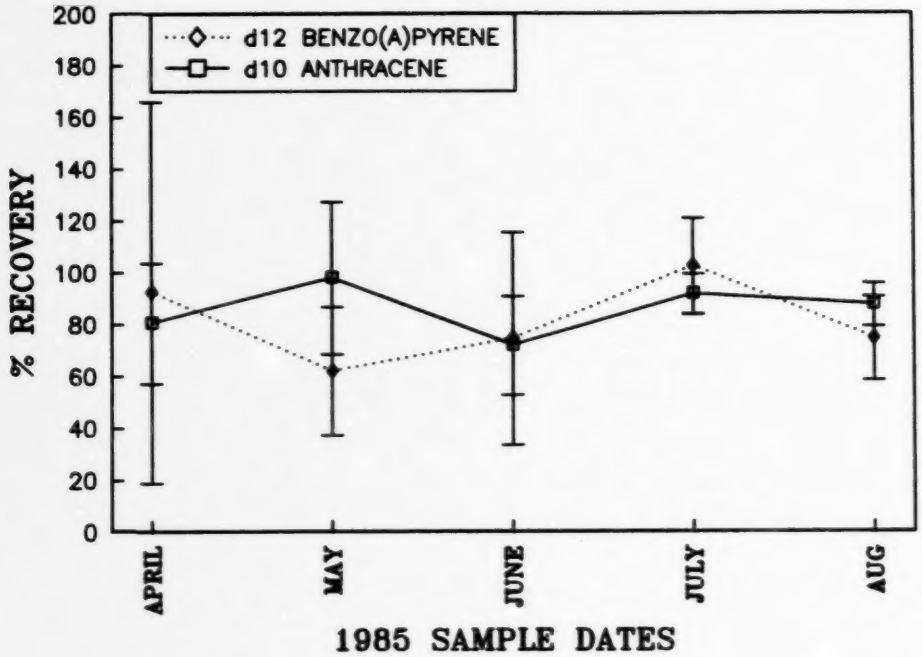

FIGURE B 2.2a RECOVERY OF PAH'S IN SITE B TOPSOIL
BLOCKS 1 AND 2

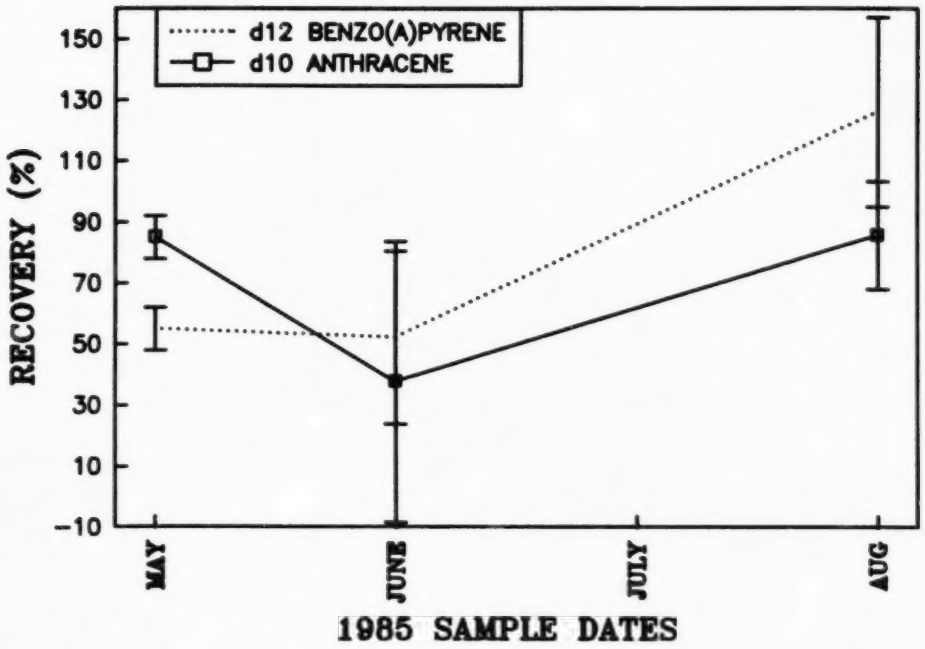

FIGURE B 2.2b RECOVERY OF PAH'S IN SITE B TOPSOIL
BLOCK 3

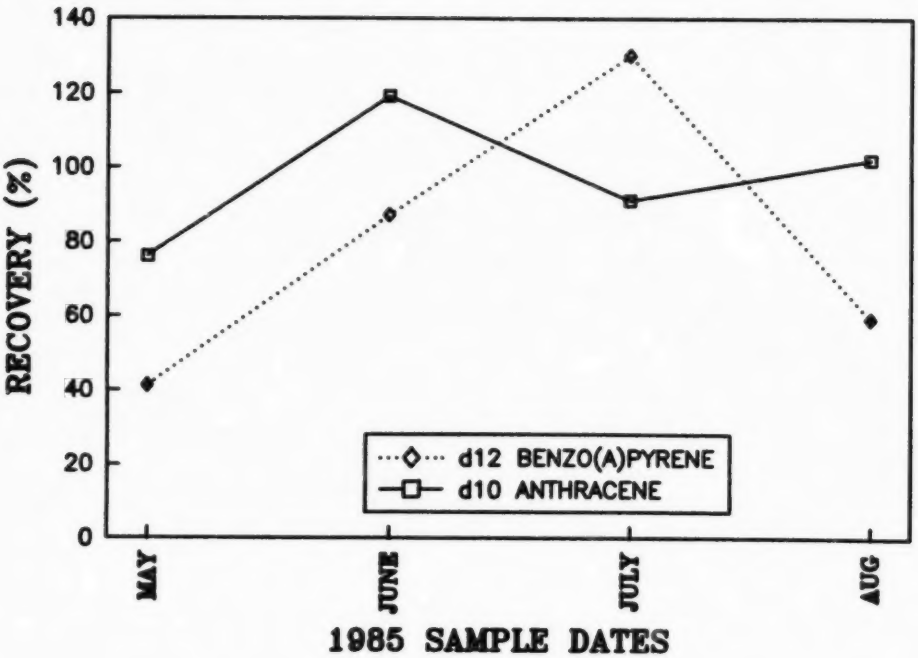

FIGURE B 2.3 RECOVERY OF PAH'S IN SITE C TOPSOIL

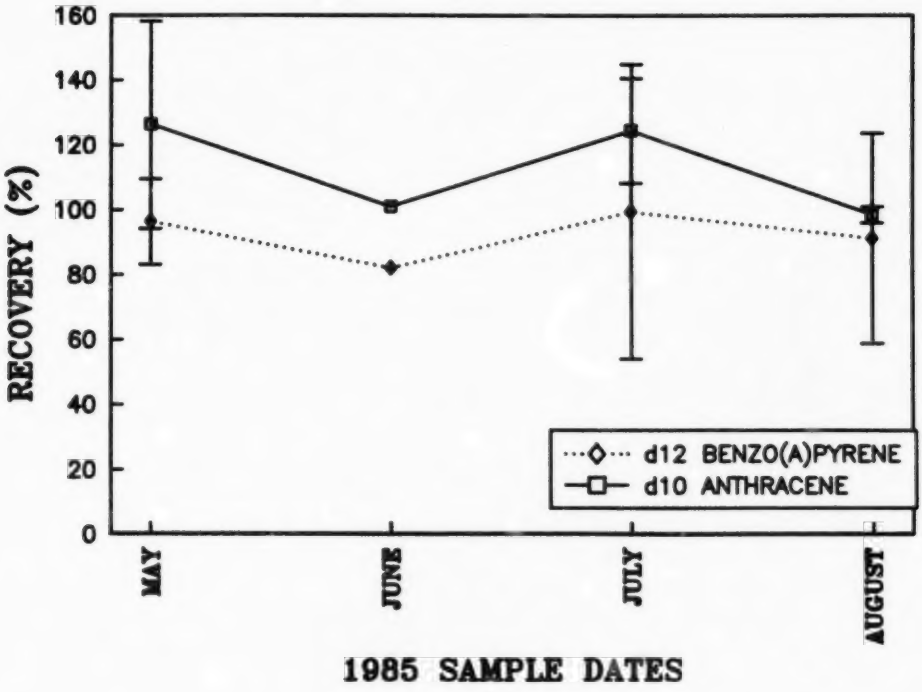
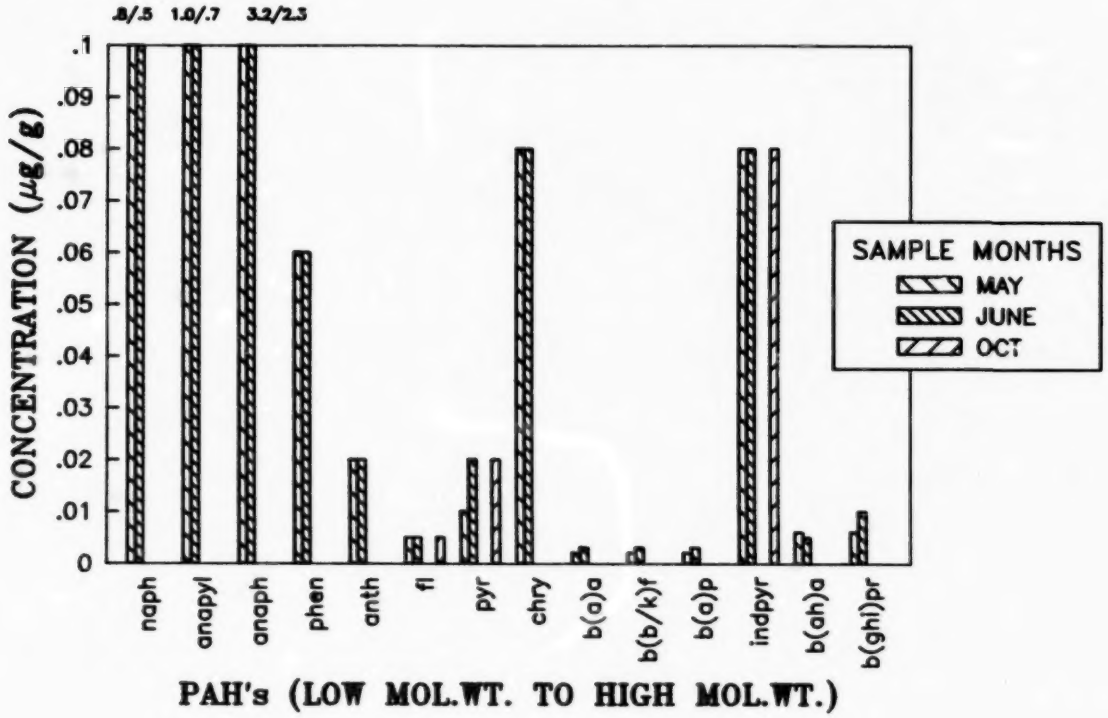
FIGURE B 2.4 DETECTION LIMITS FOR PAH'S IN WELLWATER